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COLLECTIVE OSCILLATIONS IN AN ELECTRON GAS  
OF METALLIC DENSITY. THE CORRELATION ENERGY. I

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The role of the subsidiary conditions in the Bohm and Pines theory of an electron gas is analysed anew. It is pointed out that the subsidiary conditions must be formulated in the form of two sets of operator identities: The first set establishes the Bohm-Pines operators of subsidiary conditions, and the second — the commutators of the extended Hamiltonian and of the first set. The extended Hamiltonian and the two sets of supplementary conditions are proved to be equivalent to the  $N$  electron Schrodinger equation. The two sets of subsidiary conditions enable, at last theoretically, to replace a certain number of electronic positions and momenta by coordinates and momenta of a longitudinal field describing the long-range density fluctuations. This problem cannot be solved in practice on account of mathematical difficulties. Therefore the assumption is made that a certain number of excited electron-hole pairs and the collective response to them — the rearrangement of the charge — may be described by a certain effective longitudinal field as introduced by Bohm and Pines. In the theory thus formulated, the total number of degrees of freedom of the system is correct and no subsidiary conditions are required. The Hamiltonian and the ground state function are the same as in the Bohm-Pines theory, but the number of individual electrons is smaller. The correlation energy obtained is several times smaller than that of Bohm and Pines. The theory proposed is valid within the alkali metal density range.

*1. Introduction*

In the present paper an attempt is made to elucidate what form the subsidiary conditions in the Bohm and Pines theory assume and what is their role in the collective description. This problem was discussed in several papers [1], [2], [6, 1957b], [12, 1958a], but the conclusions were controversial. Bohm and Pines formulate the subsidiary conditions in wave equation form [1], or in that of operator identities [3]. The former fails to account for the reduction in the number of degrees of freedom (in the extended Hamiltonian a certain number of new longitudinal degrees of freedom are introduced) to the value  $3N$ , as we suppose the physical system to consist of  $N$  electrons. Therefore the field of the longitudinal oscillations does not describe the



long-range charge density fluctuations, but represents some external fictitious field with which the electrons are very strongly coupled. The state vectors of such a system are non-normalizable, hence the perturbation method developed by Bohm and Pines in [1] is divergent. All this was proved in the paper [12, 1958a].

As we believe, only the subsidiary conditions in the form of operator identities are legitimate. This problem is investigated in detail in the following section.

There are two sets of subsidiary conditions: the one relates the momenta of the oscillator field to the long-range charge density fluctuations, whereas the other one relates the oscillator field coordinates to certain functions of the electron positions and momenta. The second set is not independent of the first. The simultaneous solution of both sets of subsidiary equations, i.e. the replacement of a certain number of electronic positions and momenta by oscillatory coordinates and momenta is too difficult mathematically, but this nevertheless is the only procedure ensuring that the total number of degrees of freedom of the system is conserved and simultaneously the long-range density fluctuations are represented correctly.

Since the aforementioned problem cannot be solved strictly, we formulate a new approach in section 3, consisting in the replacement of a certain number of excited electron-hole pairs and the changes in density of charge they cause by an effective oscillator field describing the long-range density fluctuations. Since now the total number of degrees of freedom is correct, the subsidiary conditions become superfluous.

A beautiful picture of collective oscillations expressed in terms of excited electron-hole pairs and individual electrons is due to Sawada, Brueckner, Brout and Fukuda [11]; their theory, however, is valid in the high density region only, whereas that presented here refers to the alkali metals. The constant in the correlation energy derived is two times smaller than that obtained by Gell-Mann and Brueckner [5] and can be further improved by perturbation treatment, since we used the ground wave function of uncoupled plasmons and individual electrons.

## 2. The subsidiary conditions in the Bohm and Pines theory

It may be useful to recapitulate the procedure adopted by Bohm and Pines in deriving their theory [1]. Let us assume a system consisting of  $N$  electrons. Instead of introducing the positive ions, which complicate mathematically all the computations, we assume the electrons to move within the volume  $V$  filled out with a uniform positive charge background. The total charge of the system is zero. All the calculations in the present paper are valid when  $N \rightarrow +\infty$ ,  $V = L^3 \rightarrow +\infty$ ,  $\frac{N}{V} = \text{const.}$  We assume the volume  $V$  to be a cube of edge  $L$ , and apply the periodic boundary conditions.

The Hamiltonian of the system is now

$$\hat{H} = \sum_{i=1}^N \frac{\hat{\mathbf{p}}_i^2}{2m} + e^2 \sum_{i < j} \frac{1}{r_{ij}} - \frac{Ne^2}{V} \sum_{i=1}^N \int \frac{d\mathbf{r}}{|\mathbf{r} - \mathbf{r}_i|} + \frac{N^2 e^2}{2V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.1)$$

wherein the third term represents the interaction energy of all electrons with the positive charge background, and the fourth — the interaction of the background with itself.

The Fourier transforms of  $1/r$  ( $r$  is the position radius) and Dirac's function are of the well known form

$$\frac{1}{r} = \frac{4\pi}{V} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{k^2}, \quad (2.2)$$

$$\delta(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (2.3)$$

It is also convenient to introduce the Kroenecker delta,

$$\delta_K(\mathbf{k}) = \begin{cases} 1, & \mathbf{k} = 0, \\ 0, & \text{otherwise.} \end{cases} \quad (2.4)$$

The charge density of the system is now

$$\varrho(\mathbf{r}) = -e \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) + \frac{Ne}{V} = \frac{1}{V} \sum_{\mathbf{k}} \varrho_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (2.5)$$

where  $Ne/V$  denotes the density of positive charge background. With respect to (2.3) and (2.5), we obtain

$$\varrho_{\mathbf{k}} = -e \sum_{i=1}^N e^{-i\mathbf{k} \cdot \mathbf{r}_i} + Ne \delta_K(\mathbf{k}), \quad (2.6)$$

since

$$\frac{Ne}{V} = \frac{Ne}{V} \sum_{\mathbf{k}} \delta_K(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (2.7)$$

Moreover,

$$\varrho_0 = -e \sum_{i=1}^N 1 + Ne = -Ne + Ne = 0. \quad (2.8)$$

Let us now transform the terms of the Hamiltonian (2.1) one by one. For this purpose we use (2.2) and (2.6).

$$\begin{aligned} e^2 \sum_{i < j} \frac{1}{r_{ij}} &= \frac{e^2}{2} \sum_{i \neq j} \frac{1}{r_{ij}} = \frac{2\pi e^2}{V} \sum_{i \neq j} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot \mathbf{r}_{ij}}}{k^2} = \frac{2\pi e^2}{V} \sum_{i,j} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot \mathbf{r}_{ij}}}{k^2} - \\ &\quad - \frac{2\pi N e^2}{V} \sum_{\mathbf{k}} \frac{1}{k^2}; \end{aligned} \quad (2.9a)$$

on the other hand,

$$\begin{aligned} \varrho_{\mathbf{k}} \varrho_{-\mathbf{k}} &= \left[ -e \sum_{j=1}^N e^{-i\mathbf{k} \cdot \mathbf{r}_j} + Ne \delta_K(\mathbf{k}) \right] \cdot \left[ -e \sum_{i=1}^N e^{i\mathbf{k} \cdot \mathbf{r}_i} + Ne \delta_K(\mathbf{k}) \right] = \\ &= e^2 \sum_{i,j} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} - N^2 e^2 \delta_K(\mathbf{k}), \end{aligned} \quad (2.9b)$$

or

$$\frac{2\pi}{V} \sum_{\mathbf{k}} \frac{q_{\mathbf{k}} q_{-\mathbf{k}}}{k^2} = \frac{2\pi e^2}{V} \sum_{i,j} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot \mathbf{r}_{ij}}}{k^2} - \frac{2\pi N^2 e^2}{V} \sum_{\mathbf{k}} \frac{\delta_K(\mathbf{k})}{k^2}, \quad (2.9c)$$

By comparing (2.9a) and (2.9c) we obtain

$$e^2 \sum_{i < j} \frac{1}{r_{ij}} = \frac{2\pi}{V} \sum_{\mathbf{k}} \frac{q_{\mathbf{k}} q_{-\mathbf{k}} - N e^2}{k^2} + \frac{2\pi N^2 e^2}{V} \sum_{\mathbf{k}} \frac{\delta_K(\mathbf{k})}{k^2}. \quad (2.9d)$$

The third term of eq. (2.1) is now

$$\begin{aligned} -\frac{N e^2}{V} \sum_{i=2}^N \int \frac{d\mathbf{r}}{|\mathbf{r} - \mathbf{r}_i|} &= -\frac{4\pi N e^2}{V^2} \sum_{i=2}^N \sum_{\mathbf{k}} \frac{e^{-i\mathbf{k} \cdot \mathbf{r}_i}}{k^2} \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \\ &= -\frac{4\pi N e^2}{V^2} \sum_{i=1}^N \sum_{\mathbf{k}} \frac{e^{-i\mathbf{k} \cdot \mathbf{r}_i}}{k^2} V \delta_K(\mathbf{k}) = -\frac{4\pi N^2 e^2}{V} \sum_{\mathbf{k}} \frac{\delta_K(\mathbf{k})}{k^2}. \end{aligned} \quad (2.9e)$$

Quite similarly, the fourth term of (2.1) is transformed as follows:

$$\begin{aligned} \frac{N^2 e^2}{2V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} &= \frac{2\pi N^2 e^2}{V^3} \sum_{\mathbf{k}} \frac{1}{k^2} \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \int d\mathbf{r}' e^{-i\mathbf{k} \cdot \mathbf{r}'} \\ &= \frac{2\pi N^2 e^2}{V^3} \sum_{\mathbf{k}} \frac{1}{k^2} V^2 \delta_K(\mathbf{k}) = \frac{2\pi N^2 e^2}{V} \sum_{\mathbf{k}} \frac{\delta_K(\mathbf{k})}{k^2}. \end{aligned} \quad (2.9f)$$

Collecting all transformed terms we get

$$\begin{aligned} \hat{H} &= \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + \frac{2\pi}{V} \sum_{\mathbf{k}} \frac{q_{\mathbf{k}} q_{-\mathbf{k}} - N e^2}{k^2} + \left( \frac{2\pi N^2 e^2}{V} - \frac{4\pi N^2 e^2}{V} + \right. \\ &\quad \left. + \frac{2\pi N^2 e^2}{V} \right) \sum_{\mathbf{k}} \frac{\delta_K(\mathbf{k})}{k^2} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + \frac{2\pi}{V} \sum_{\mathbf{k}} \frac{q_{\mathbf{k}} q_{-\mathbf{k}} - N e^2}{k^2}, \quad \hat{H}\Psi = E\Psi. \end{aligned} \quad (2.10)$$

This is modified form of Schroedinger's equation for the system of  $N$  electrons and positive charge background.

Such a system of particles may also be described by the longitudinal field represented by the vector potential

$$\vec{A}(\mathbf{r}) = \sqrt{\frac{4\pi c^2}{V}} \sum_{|\mathbf{k}| \leq k_c} q_{\mathbf{k}} \vec{\epsilon}_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}, \quad \vec{\epsilon}_{\mathbf{k}} = \frac{\mathbf{k}}{k}, \quad (2.11)$$



where  $c$  is the velocity of light and  $q_k$  are coordinates of the field. The electric vector is now

$$\vec{E}(\mathbf{r}) = -\frac{1}{c} \frac{\partial}{\partial t} \vec{A}(\mathbf{r}) = -\sqrt{\frac{4\pi}{V}} \sum_{|\mathbf{k}| \leq k_c} \frac{\partial q_k}{\partial t} \vec{\varepsilon}_k e^{i\mathbf{k} \cdot \mathbf{r}} = \sqrt{\frac{4\pi}{V}} \sum_{|\mathbf{k}| \leq k_b} p_{-k} \vec{\varepsilon}_k e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (2.12)$$

with  $p_k$  as momentum of the longitudinal field.

With respect to (2.11) and (2.12), we have

$$\begin{aligned} \hat{H}_{\text{new}} = & \frac{1}{2m} \sum_{i=1}^N \left( \hat{\mathbf{p}}_i + \frac{e}{c} \vec{A}_i \right)^2 + \frac{2\pi}{V} \sum_{|\mathbf{k}| > k_c} \frac{q_k q_{-k} - Ne^2}{k^2} - \frac{1}{8\pi} \int d\mathbf{r} E^2(\mathbf{r}) - \\ & - \frac{2\pi Ne^2}{V} \sum_{|\mathbf{k}| \leq k_c} \frac{1}{k^2}. \end{aligned} \quad (2.13)$$

We postulate now that Maxwell's equation be satisfied:

$$[\text{div } \vec{E}(\mathbf{r}) - 4\pi Q(\mathbf{r})]_{\mathbf{k}} = 0, \quad (2.14a)$$

or

$$\Omega_{\mathbf{k}}^{(1)} = p_{-k} - i \sqrt{\frac{4\pi}{V k^2}} q_k = 0, \quad |\mathbf{k}| \leq k_c. \quad (2.14b)$$

The subsidiary conditions (2.14b) relate the momenta  $p_{-k}$  to the long-range Fourier transforms of charge density, i. e. to the functions of all electronic positions. Let us write the conditions in explicit form

$$\Omega_{\mathbf{k}}^{(1)} = p_{-k} + ie \sqrt{\frac{4\pi}{V k^2}} \sum_{i=1}^N e^{-i\mathbf{k} \cdot \mathbf{r}_i} = 0, \quad |\mathbf{k}| \leq k_c. \quad (2.15)$$

Were we able to solve these equations, it would be possible to replace the  $n'/3$  electronic positions ( $n'$  is the number of all  $\mathbf{k}$  within the interval  $|\mathbf{k}| \leq k_c$ ) by  $n'$  oscillator field momenta, but such a solution of the problem cannot be obtained.

Let us now rewrite the Hamiltonian (2.13) in the more developed form using (2.11) and (2.12),

$$\begin{aligned} \hat{H}_{\text{new}} = & \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} + \frac{2\pi}{V} \sum_{|\mathbf{k}| > k_c} \frac{q_k q_{-k} - Ne^2}{k^2} - \frac{1}{2} \sum_{|\mathbf{k}| \leq k_c} (p_k p_{-k} + \omega_p^2 q_k q_{-k}) + \\ & + \frac{e}{m} \sqrt{\frac{4\pi}{V}} \sum_{i=1}^N \sum_{|\mathbf{k}| \leq k_c} q_k \vec{\varepsilon}_k \cdot (\hat{\mathbf{p}}_i - \hbar \mathbf{k}/2) e^{i\mathbf{k} \cdot \mathbf{r}_i} - \frac{2\pi N e^2}{V} \sum_{|\mathbf{k}| \leq k_c} \frac{1}{k^2} + \\ & + \frac{2\pi e^2}{mV} \sum_{\substack{|\mathbf{k}| \leq k_c \\ |\mathbf{k}'| \leq k_c \\ \mathbf{k} + \mathbf{k}' \neq 0}} q_k q_{k'} \vec{\varepsilon}_k \cdot \vec{\varepsilon}_{k'} \sum_{i=1}^N e^{i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}_i}, \quad \omega_p^2 = \frac{4\pi N e^2}{mV}. \end{aligned} \quad (2.16)$$

It must be

$$[\hat{H}_{new}, \Omega_{-k}^{(1)}] = 0, \quad |\mathbf{k}| \leq k_c. \quad (2.17)$$

This is legitimate, since  $\Omega_k^{(1)}$ , according to (2.15), is the zero operator. Straightforward computation yields

$$\begin{aligned} [\hat{H}_{new}, \Omega_{-k}^{(1)}] = & \frac{2ie\hbar}{m} \sqrt{\frac{4\pi}{V}} \sum_{i=1}^N \left[ \varepsilon_k \cdot (\hat{p}_i - \hbar \mathbf{k}/2) e^{i\mathbf{k} \cdot \mathbf{r}_i} + \right. \\ & \left. + e \sqrt{\frac{4\pi}{V}} \sum_{|\mathbf{k}'| \leq k_c} q_{\mathbf{k}'} \vec{\varepsilon}_k \cdot \vec{\varepsilon}_{\mathbf{k}'} e^{i(\mathbf{k}+\mathbf{k}') \cdot \mathbf{r}_i} \right] = 0 \end{aligned} \quad (2.18a)$$

or

$$\begin{aligned} \Omega_k^{(2)} = & \sum_{i=1}^N \vec{\varepsilon}_k \cdot (\hat{p}_i - \hbar \mathbf{k}/2) e^{i\mathbf{k} \cdot \mathbf{r}_i} + \\ & + e \sqrt{\frac{4\pi}{V}} \sum_{|\mathbf{k}'| \leq k_c} q_{\mathbf{k}'} \vec{\varepsilon}_k \cdot \vec{\varepsilon}_{\mathbf{k}'} \sum_{i=1}^N e^{i(\mathbf{k}+\mathbf{k}') \cdot \mathbf{r}_i} = 0, \quad |\mathbf{k}| \leq k_c \end{aligned} \quad (2.18b)$$

This is the second set of subsidiary equations relating the oscillator field coordinates to the electronic momenta and positions. The solution of these equations, if achievable, would replace the  $n'/3$  electron momenta by the longitudinal coordinates  $q_{\mathbf{k}}$  (we assume the  $n'$  selected  $\mathbf{r}_i$  to have been replaced by the momenta  $p_{\mathbf{k}}$ ). In this way two sets of subsidiary conditions would yield the  $3N - n'$  electronic and  $n'$  plasmon degrees of freedom. But this programme is mathematically too difficult for execution.

The physical equivalence of the Hamiltonian (2.16) together with the subsidiary equations (2.15) and (2.18b) and of the Hamiltonian (2.10) is easily proved. The proof is along the following lines:

$$p_{\mathbf{k}} = i \sqrt{\frac{4\pi}{V}} q_{-\mathbf{k}}, \quad p_{-\mathbf{k}} = i \sqrt{\frac{4\pi}{V}} q_{\mathbf{k}}, \quad |\mathbf{k}| \leq k_c,$$

whence

$$-\frac{1}{2} \sum_{|\mathbf{k}| \leq k_c} p_{\mathbf{k}} p_{-\mathbf{k}} = \frac{2\pi}{V} \sum_{|\mathbf{k}| \leq k_c} \frac{q_{\mathbf{k}} q_{-\mathbf{k}}}{k^2}. \quad (2.19a)$$

By (2.18b) we have

$$\sum_{i=1}^N \vec{\varepsilon}_k \cdot (\hat{p}_i - \hbar \mathbf{k}/2) e^{i\mathbf{k} \cdot \mathbf{r}_i} + e \sqrt{\frac{4\pi}{V}} \sum_{|\mathbf{k}'| \leq k_c} q_{\mathbf{k}'} \vec{\varepsilon}_k \cdot \vec{\varepsilon}_{\mathbf{k}'} \sum_{i=1}^N e^{i(\mathbf{k}+\mathbf{k}') \cdot \mathbf{r}_i} = 0, \quad |\mathbf{k}| \leq k_c.$$

Multiplication of the last equation by  $\frac{e}{m} \sqrt{\frac{4\pi}{V}} q_{\mathbf{k}}$  and summation over  $|\mathbf{k}| \leq k_c$



(the double sum over  $\mathbf{k}$  and  $\mathbf{k}'$  must be multiplied by 1/2 to avoid repetitions in  $\mathbf{k}$ ) yields

$$\begin{aligned}
 & \frac{e}{m} \sqrt{\frac{4\pi}{V}} \sum_{i=1}^N \sum_{|\mathbf{k}| \leq k_c} q_k \vec{\epsilon}_k \cdot (\hat{\mathbf{p}}_i - \hbar \mathbf{k}/2) e^{i\mathbf{k} \cdot \mathbf{r}_i} + \frac{2\pi e^2}{mV} \sum_{\substack{|\mathbf{k}| \leq k_c \\ |\mathbf{k}'| \leq k_c}} q_k q_{k'} \vec{\epsilon}_k \cdot \vec{\epsilon}_{k'} \sum_{i=1}^N e^{i(\mathbf{k}+\mathbf{k}') \cdot \mathbf{r}_i} \\
 &= \frac{e}{m} \sqrt{\frac{4\pi}{V}} \sum_{i=1}^N \sum_{|\mathbf{k}| \leq k_c} q_k \vec{\epsilon}_k \cdot (\vec{\mathbf{p}}_i - \hbar \mathbf{k}/2) e^{i\mathbf{k} \cdot \mathbf{r}_i} - \frac{1}{2} \sum_{|\mathbf{k}| \leq k_c} \omega_p^2 q_k q_{-k} + \frac{2\pi e^2}{mV} \times \\
 & \quad \times \sum_{\substack{|\mathbf{k}| \leq k_c \\ |\mathbf{k}'| \leq k_c \\ \mathbf{k}+\mathbf{k}' \neq 0}} q_k q_{k'} \vec{\epsilon}_k \cdot \vec{\epsilon}_{k'} \sum_{i=1}^N e^{i(\mathbf{k}+\mathbf{k}') \cdot \mathbf{r}_i} = 0. \tag{2.19b}
 \end{aligned}$$

With respect to (2.19a) and (2.19b), the Hamiltonian (2.16) is of course identical with one of (2.10).

In the paper [1] Bohm and Pines postulate the subsidiary conditions in form of the wave equation

$$\Omega_k^{(1)} \Psi = 0, \quad |\mathbf{k}| \leq k_c, \tag{2.20}$$

where  $\Omega_k^{(1)}$  is given by (2.15). Such equations are satisfied by non-normalizable state vectors, as proved by Kanazawa [6, 1957b]. Moreover, the principal requirement, which consists in the reduction of the  $3N + n'$  degrees of freedom to  $3N$  is not fulfilled by such subsidiary conditions, hence the solutions of (2.20) describe the behaviour of  $N$  electrons in some fictitious external field. The interaction of electrons with such a field is very strong, as computed by the present author [12, 1958a]. Thus, obviously, the perturbation-theoretic treatment of the problem given by Bohm and Pines [1] is fruitless. If we require only

$$\Omega_k^{(1)} = 0, \quad |\mathbf{k}| \leq k_c, \tag{2.15}$$

the theory is freed of aforementioned difficulties, since now some electronic degrees of freedom are replaced by other ones, which also are internal. The formulation of subsidiary conditions in the form of (2.15) was investigated by Bohm [3].

### 3. Collective oscillations in an electron gas. The correlation energy

Suppose we have  $N$  electrons immersed in a medium of uniform positive charge within a cube of volume  $V$ . Let us at first assume that the electrons do not interact and that they are regularly distributed over the entire space of the system. By regular distribution we understand that any one of the  $N$  electrons is nearly at centre of „its” cell  $V/N$ . The Fourier charge density transform is now nearly zero. Let us now very slowly (adiabatically) to “switch on” the interactions between the electrons until they attain their real values. Since there are locally slight differences of charge density, these increase with the increase in interaction. Finally a certain number of

electrons enter into collision, giving rise to local charge unbalance imitating an excited electron-hole pair (the "hole" is here the unbalanced locally part of the positive charge background). The system as a whole meets the appearance of such pairs with collective response, i.e. with some kind of rearrangement of charge. Both interconnected phenomena, namely, the arising of a certain number, say  $n'/3$ , of pairs and the new distribution of charge depending thereon will be described with the help of an effective longitudinal field given by the vector potential

$$\vec{A}(\mathbf{r}) = \sqrt{\frac{4\pi c^2}{V}} \sum_{|\mathbf{k}| \leq k_c} q_k \vec{\varepsilon}_k e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (3.1)$$

We assume that the state of the system is such that there are  $N - n'/3$  individual electrons and  $n'$  field coordinates  $q_k$  responsible for the  $n'/3$  excited pairs and for the related rearrangement of charge. We further assume the state of the system to be "stationary", i.e. that  $n'$  depends only on the temperature and the mean distance between the electrons.

We now write the Hamiltonian of our system:

$$\begin{aligned} \hat{H} = & \frac{1}{2m} \sum_{i=1}^{N'} (\hat{\mathbf{p}}_i + \frac{e}{c} \vec{A}_i)^2 + \frac{2\pi}{V} \sum_{|\mathbf{k}| > k_c} \frac{q_k q_{-k} - N' e^2}{k^2} - \frac{1}{8\pi} \int d\mathbf{r} E^2(\mathbf{r}) - \\ & - \frac{2\pi N' e^2}{V} \sum_{|\mathbf{k}| \leq k_c} \frac{1}{k^2} - \frac{N' e^2}{V} \sum_{i=1}^{N'} \int \frac{d\mathbf{r}}{|\mathbf{r} - \mathbf{r}_i|} + \frac{N'^2 e^2}{2V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \end{aligned} \quad (3.2)$$

wherein

$$\vec{E}(\mathbf{r}) = \sqrt{\frac{4\pi}{V}} \sum_{|\mathbf{k}| \leq k_c} p_{-k} \varepsilon_k e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (3.3)$$

Moreover,

$$N' = N - n'/3, \quad (3.4)$$

$$n' = \sum_{|\mathbf{k}| \leq k_c}. \quad (3.5)$$

The second term in eq. (3.2) represents the short-range Coulomb interaction between the electrons, since it may be additionally assumed that the rearrangement of charge due to the excited pairs produces screening in the Coulomb interactions of the individual electrons.

The total number of degrees of freedom is now correct:

$$3(N - n'/3) \text{ electronic plus } n' \text{ of the field} = 3N. \quad (3.6)$$

In equation (3.1) we include  $\mathbf{k} = 0$ ,

$$\vec{A}(\mathbf{r}) = \sqrt{\frac{4\pi c^2}{V}} \sum'_{|\mathbf{k}| \leq k_c} q_k \vec{\varepsilon}_k e^{i\mathbf{k} \cdot \mathbf{r}} + \sqrt{\frac{4\pi c^2}{V}} q_0 \hat{z}^0, \quad (3.7)$$

where prime in the sum over  $\mathbf{k}$  denotes the dropping of  $\mathbf{k} = 0$ , and the constant  $q_0$  will be determined later on.  $\hat{z}^0$  is the unit vector along the  $z$  — axis.

By (3.2) and (3.3), the explicite form of the Hamiltonian (3.2) is now

$$\begin{aligned}
\hat{H} = & \sum_{i=1}^{N'} \frac{\hat{p}_i^2}{2m} + e^2 \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \left( 1 - \frac{2}{\pi} \int_0^{\bar{k}_c |\mathbf{r}_i - \mathbf{r}_j|} d\tau \frac{\sin \tau}{\tau} \right) - \frac{1}{2} \sum_{|\mathbf{k}| \leq \bar{k}_c} (p_k p_{-k} + \\
& + \omega_p^2 q_k q_{-k}) + \frac{e}{m} \sqrt{\frac{4\pi}{V}} \sum_{i=1}^{N'} \sum_{|\mathbf{k}| \leq \bar{k}_c} q_k \vec{\varepsilon}_k \cdot (\vec{p}_i - \hbar \mathbf{k}/2) e^{i\mathbf{k} \cdot \mathbf{r}_i} + \\
& + \frac{2\pi e^2}{mV} \sum_{i=1}^{N'} \sum_{\substack{|\mathbf{k}| \leq \bar{k}_c \\ |\mathbf{k}'| \leq \bar{k}_c \\ \mathbf{k} + \mathbf{k}' \neq 0}} q_k q_{k'} \vec{\varepsilon}_k \cdot \vec{\varepsilon}_{k'} e^{i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}_i} + \frac{4\pi e^2}{mV} q_0 \sum_{i=1}^{N'} \sum_{|\mathbf{k}| \leq \bar{k}_c} q_k \mathcal{Z}^0 \cdot \vec{\varepsilon}_k e^{i\mathbf{k} \cdot \mathbf{r}_i} + \\
& + \frac{2\pi N' e^2}{mV} q_0^2 - \frac{2\pi N' e^2}{V} \sum_{|\mathbf{k}| \leq \bar{k}_c} \frac{1}{k^2} - \frac{N' e^2}{V} \sum_{i=1}^{N'} \int \frac{d\mathbf{r}}{|\mathbf{r} - \mathbf{r}_i|} + \\
& + \frac{N'^2 e^2}{2V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad \omega_p^2 = \frac{4\pi N' e^2}{mV}, \tag{3.8}
\end{aligned}$$

We write the ground state function of the system as follows:

$$\Psi = \frac{1}{\sqrt{N'!}} \Phi_0 \begin{vmatrix} \varphi_{k_1}(\mathbf{r}_1) \eta_+(\sigma_1), & \dots, & \varphi_{k_1}(\mathbf{r}_{N'}) \eta_+(\sigma_{N'}) \\ \vdots & & \vdots \\ \eta_{k_{n_r}}(\mathbf{r}_1) \eta_+(\sigma_1), & \dots, & \varphi_{k_{n_r}}(\mathbf{r}_{N'}) \eta_+(\sigma_{N'}) \\ \varphi_{k_{n_r+1}}(\mathbf{r}_1) \eta_-(\sigma_1), & \dots, & \varphi_{k_{n_r+1}}(\mathbf{r}_{N'}) \eta_-(\sigma_{N'}) \\ \vdots & & \vdots \\ \varphi_{k_{N'}}(\mathbf{r}_1) \eta_-(\sigma_1), & \dots, & \varphi_{k_{N'}}(\mathbf{r}_{N'}) \eta_-(\sigma_{N'}) \end{vmatrix}, \tag{3.9}$$

where  $\Phi_0$  is the oscillatory vacuum vector,  $\eta_+(\sigma_i)$ ,  $\eta_-(\sigma_i)$  stand for right spin respectively left spin functions,  $n_r$  is the number of right spins, and

$$\varphi_k(\mathbf{r}) = \frac{1}{V^{1/2}} e^{i\mathbf{k} \cdot \mathbf{r}}. \tag{3.10}$$

We shall investigate the two magnetic possibilities only, namely

$$n_r = \vartheta N' = \begin{cases} \vartheta = 1/2, & \text{non-magnetic state,} \\ \vartheta = 1, & \text{magnetic state.} \end{cases} \tag{3.11}$$

In connection with eq. (3.6) we introduce the Fermi distribution for absolute zero temperature

$$V \cdot \frac{4\pi}{3} k_F^3 = (2\pi)^3 N' \vartheta, \tag{3.12}$$

wherein  $k_F$  is the wave vector of the Fermi surface.



The Fermi distribution for the  $N$  electron problem (without plasmons) is of the form

$$V \cdot \frac{4\pi}{3} k_0^3 = (2\pi)^3 N \vartheta. \quad (3.13)$$

$k_0$  now depends on  $N$ .

The number of longitudinal degrees of freedom  $n^*$  will be

$$n^* = \sum_{|\mathbf{k}| \leq k_c} = \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_c} d\mathbf{k} = \frac{V}{2\pi^2} \int_0^{k_c} dk \cdot k^2 = \frac{V k_c^3}{3! \pi^2}. \quad (3.14)$$

The quantity  $n^*$  or  $k_c$  is the variational parameter of our problem. It will be more convenient, however, to solve the variational problem with

$$\beta = \frac{k_c}{k_0} < 1, \quad (3.15)$$

and not directly with  $k_c$ .

By (3.4), (3.12), (3.13) and (3.14), (3.15), we obtain

$$\frac{N^*}{N} = 1 - \frac{n^*}{3N} = 1 - \frac{V k_0^3}{N} \frac{\beta^3}{3 \cdot 3! \pi^2} = 1 - \frac{\vartheta}{3} \beta^3, \quad (3.16)$$

$$\frac{k_F}{k_0} = \left( 1 - \frac{\vartheta}{3} \beta^3 \right)^{1/3}. \quad (3.17)$$

We now introduce the spacing parameter  $r_s$  by the equation

$$N \frac{4\pi}{3} a_0^3 r_s^3 = V, \quad (3.18)$$

with  $a_0$  denoting the Bohr radius, and by combining eq. (3.18) with (3.13) we get

$$k_0 = \left( \frac{9\pi\vartheta}{2} \right)^{1/3} \frac{1}{r_s} \frac{me^2}{\hbar^2}. \quad (3.19)$$

Let us now compute the mean kinetic energy per one individual particle in state (3.9) and on the average over the Fermi distribution (3.12). We have

$$\begin{aligned} T &= \frac{1}{N} \left\langle \left( \Psi^*, \sum_{i=1}^{N^*} \frac{\hat{p}_i^2}{2m} \Psi \right) \right\rangle = \frac{\hbar^2}{2m} \frac{\int d\mathbf{k} \cdot k^2}{\int d\mathbf{k}} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} \\ &= \frac{3}{5} \frac{\hbar^2 k_0^2}{2m} \left( \frac{k_F}{k_0} \right)^2 = \frac{3}{5} \left( \frac{9\pi\vartheta}{2} \right)^{2/3} \left( 1 - \frac{\vartheta}{3} \beta^3 \right)^{2/3} \frac{1}{r_s^2} \frac{me^4}{2\hbar^2} \\ &= \frac{3}{5} \left( \frac{9\pi\vartheta}{2} \right)^{2/3} \left( 1 - \frac{\vartheta}{3} \beta^3 \right)^{2/3} \frac{1}{r_s^2} \text{ Ry}. \end{aligned} \quad (3.20)$$

We have utilized (3.17) and (3.19) and expressed the energy in Rydbergs. For the non-magnetic and magnetic state we obtain, respectively,

$$T_{\uparrow\downarrow} = \frac{2.2100}{r_s^2} \left(1 - \frac{1}{6} \beta^3\right)^{\frac{2}{3}} \text{ Ry}, \quad (3.21)$$

$$T_{\uparrow\uparrow} = \frac{3.5077}{r_s^2} \left(1 - \frac{1}{3} \beta^3\right)^{\frac{2}{3}} \text{ Ry}. \quad (3.22)$$

In order to compute the mean of the oscillator part of the Hamiltonian (3.8) we notice that

$$\begin{aligned} p_k &= i \left( \frac{\hbar \omega_p}{2} \right)^{\frac{1}{2}} (a_{-k} + a_k^*), \\ q_k &= \left( \frac{\hbar}{2\omega_p} \right)^{\frac{1}{2}} (a_k - a_{-k}^*), \quad \mathbf{k} \neq 0, \end{aligned} \quad (3.23)$$

where  $a_k$ ,  $a_k^*$  are annihilation and creation oscillator operators. Since the vacuum vector is defined by equations

$$a_k \Phi_0 = 0, \quad \Phi_0^* a_k^* = 0, \quad (3.24)$$

we have

$$\Phi_0^* q_k \Phi_0 = 0, \quad \Phi_0^* p_k \Phi_0 = 0. \quad (3.25)$$

Moreover

$$\hat{H}_{\text{osc}} = -\frac{1}{2} \sum_{|\mathbf{k}| \leq k_c} (p_k p_{-k} + \omega_p^2 q_k q_{-k}) = \sum_{|\mathbf{k}| \leq k_c} \hbar \omega_p (a_k^* a_k + 1/2), \quad (3.26)$$

whence

$$-\frac{1}{2} \sum_{|\mathbf{k}| \leq k_c} \Phi_0^* (p_k p_{-k} + \omega_p^2 q_k q_{-k}) \Phi_0 = \sum_{|\mathbf{k}| \leq k_c} \frac{\hbar \omega_p}{2} = \frac{\hbar \omega_p}{2} n'. \quad (3.27)$$

By (3.14), (3.15), (3.16) and (3.17) we obtain per one electron,

$$\begin{aligned} E_{\text{osc}} &= \frac{1}{N} (\Psi^*, \hat{H}_{\text{osc}} \Psi) = \frac{1}{N} \Phi_0^* \hat{H}_{\text{osc}} \Phi_0 = \frac{\hbar \omega_p n'}{2N} \\ &= \frac{V k_0^3}{N} \frac{\hbar \omega_p}{2 \cdot 3! \pi^2} \left( \frac{N}{N^3} \right) \beta^3 = \frac{\hbar \omega_p}{2} \frac{\partial}{1 - \frac{\partial}{3} \beta^3} \beta^3. \end{aligned}$$

$E_{\text{osc}}$  expressed in Rydbergs is

$$E_{\text{osc}} = \frac{\hbar \omega_p}{e^2/a_0} \frac{\partial \beta^3}{\left(1 - \frac{\partial}{3} \beta^3\right)} \text{ Ry}. \quad (3.28)$$

The quotient  $\hbar\omega_p a_0/e^2$  can be transformed as follows:

$$\begin{aligned} \left( \frac{\hbar\omega_p a_0}{e^2} \right)^2 &= \frac{\hbar^2 4\pi N' e^2 a_0^2}{m V e^4} = 4\pi a_0^3 \frac{N'}{V} = 4\pi a_0^3 \frac{N}{V} \frac{N'}{N} = \frac{4\pi a_0^3}{3} \left( 1 - \frac{\vartheta}{3} \beta^3 \right) \\ &= \frac{3}{r_s^3} \left( 1 - \frac{\vartheta}{3} \beta^3 \right). \end{aligned}$$

Finally,

$$\frac{\hbar\omega_p}{e^2/a_0} = \frac{\sqrt{3}}{r_s^{3/2}} \left( 1 - \frac{\vartheta}{3} \beta^3 \right)^{1/2}$$

and

$$E_{\text{osc}} = \frac{\sqrt{3}}{r_s^{3/2}} \frac{\vartheta \beta^3}{\left( 1 - \frac{\vartheta}{3} \beta^3 \right)^{1/2}} \text{ Ry.}$$

Thus, we have

$$E_{\text{osc}}^{\uparrow\downarrow} = \frac{\sqrt{3}}{2r_s^{3/2}} \frac{\beta^3}{\left( 1 - \frac{1}{6} \beta^3 \right)^{1/2}} \text{ Ry,} \quad (3.29)$$

$$E_{\text{osc}}^{\uparrow\uparrow} = \frac{\sqrt{3}}{r_s^{3/2}} \frac{\beta^3}{\left( 1 - \frac{1}{3} \beta^3 \right)^{1/2}} \text{ Ry.} \quad (3.30)$$

The mean value of the fourth, fifth and sixth terms of the Hamiltonian (3.8) is zero owing to eq. (3.25). The zero component of the fourth term

$$\frac{e}{m} \sqrt{\frac{4\pi}{V}} q_0 \sum_{i=1}^{N'} z^0 \cdot \hat{\mathbf{p}}_i$$

vanishes since the Fermi distribution is isotropic in momentum directions.

The long-range self energy term  $-\frac{2\pi N' e^2}{V} \sum_{|\mathbf{k}| \leq k_c} 1/k^2$  is, per one particle,

$$\begin{aligned} E_s &= -\frac{2\pi e^2}{V} \sum_{|\mathbf{k}| \leq k_c} \frac{1}{k^2} = -\frac{e^2}{4\pi^2} \int_{|\mathbf{k}| \leq k_c} \frac{d\mathbf{k}}{k^2} = -\frac{e^2 k_c}{\pi} = -\frac{e^2 k_0 \beta}{\pi} \\ &= -\frac{2}{\pi} \left( \frac{9\pi\vartheta}{2} \right)^{1/3} \frac{\beta}{r_s} \frac{m e^4}{2\hbar^2} = -\frac{2}{\pi} \left( \frac{9\pi\vartheta}{2} \right)^{1/3} \frac{\beta}{r_s} \text{ Ry,} \end{aligned}$$

$$E_s^{\uparrow\downarrow} = -\frac{1.2217}{r_s} \beta \text{ Ry,} \quad (3.31)$$

$$E_s^{\uparrow\uparrow} = -\frac{1.5392}{r_s} \beta \text{ Ry.} \quad (3.32)$$



Let us now examine the screened Coulomb interaction term in (3.8). For this purpose, we compute the following mean value:

$$\left( \Psi^*, \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r}_1 - \mathbf{r}_2|} d\tau \frac{\sin \tau}{\tau} \right) \Psi \right).$$

By (3.9), we have,

$$\begin{aligned} \Psi = & \frac{1}{\sqrt{N!}} \Phi_0 \left[ \sum_{l < p}^{(+)} \left| \begin{matrix} \varphi_{k_l}(\mathbf{r}_1), & \varphi_{k_l}(\mathbf{r}_2) \\ \varphi_{k_p}(\mathbf{r}_1), & \varphi_{k_p}(\mathbf{r}_2) \end{matrix} \right| \eta_+(\sigma_1) \eta_+(\sigma_2) \Psi^{lp; 12} + \right. \\ & + \sum_{l < p}^{(-)} \left| \begin{matrix} \varphi_{k_l}(\mathbf{r}_1), & \varphi_{k_l}(\mathbf{r}_2) \\ \varphi_{k_p}(\mathbf{r}_1), & \varphi_{k_p}(\mathbf{r}_2) \end{matrix} \right| \eta_-(\sigma_1) \eta_-(\sigma_2) \Psi^{lp; 12} + \\ & \left. \sum_l^{(+)} \sum_p^{(-)} \left| \begin{matrix} \varphi_{k_l}(\mathbf{r}_1) \eta_+(\sigma_1), & \varphi_{k_l}(\mathbf{r}_2) \eta_+(\sigma_2) \\ \varphi_{k_p}(\mathbf{r}_1) \eta_-(\sigma_1), & \varphi_{k_p}(\mathbf{r}_2) \eta_-(\sigma_2) \end{matrix} \right| \Psi^{lp; 12} \right], \end{aligned}$$

wherein the  $\Psi^{lp; 12}$  denote the minors (including sign) of the determinant (3.9) obtained by deleting therein the  $l$ -th and  $p$ -th lines and the first and second columns. Summa-

$\sum^{(+)}$  or  $\sum^{(-)}$  runs over right or left spin indices.

On account of the orthogonality of the functions (3.10), we obtain

$$\begin{aligned} (\Psi^{*lp; 12}, \Psi^{uv; 12}) &= \sum_{\sigma_3, \dots, \sigma_N} \int d\mathbf{r}_3 \dots \int d\mathbf{r}_N \Psi^{*lp; 12} \Psi^{uv; 12} \\ &= (N-2)! \delta_{l,u} \delta_{p,v}; \quad l < p, \quad u < v, \end{aligned} \quad (3.33a)$$

hence

$$\begin{aligned} & \left( \Psi^*, \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r}_1 - \mathbf{r}_2|} d\tau \frac{\sin \tau}{\tau} \right) \Psi \right) \\ &= \frac{1}{N!} \sum_{\sigma_1, \dots, \sigma_N} \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N \left[ \sum_{l < p}^{(+)} \left| \begin{matrix} \varphi_{k_l}^*(\mathbf{r}_1), & \varphi_{k_l}^*(\mathbf{r}_2) \\ \varphi_{k_p}^*(\mathbf{r}_1), & \varphi_{k_p}^*(\mathbf{r}_2) \end{matrix} \right| \times \right. \\ & \times \eta_+^*(\sigma_1) \eta_+^*(\sigma_2) \Psi^{*lp; 12} + \sum_{l < p}^{(-)} \left| \begin{matrix} \varphi_{k_l}^*(\mathbf{r}_1), & \varphi_{k_l}^*(\mathbf{r}_2) \\ \varphi_{k_p}^*(\mathbf{r}_1), & \varphi_{k_p}^*(\mathbf{r}_2) \end{matrix} \right| \eta_-^*(\sigma_1) \eta_-^*(\sigma_2) \Psi^{*lp; 12} + \\ & + \sum_l^{(+)} \sum_p^{(-)} \left| \begin{matrix} \varphi_{k_l}^*(\mathbf{r}_1) \eta_+^*(\sigma_1), & \varphi_{k_l}^*(\mathbf{r}_2) \eta_+^*(\sigma_2) \\ \varphi_{k_p}^*(\mathbf{r}_1) \eta_-^*(\sigma_1), & \varphi_{k_p}^*(\mathbf{r}_2) \eta_-^*(\sigma_2) \end{matrix} \right| \Psi^{*lp; 12} \left. \right] \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r}_1 - \mathbf{r}_2|} d\tau \frac{\sin \tau}{\tau} \right) \times \\ & \times \left[ \sum_{u < v}^{(+)} \left| \begin{matrix} \varphi_{k_u}(\mathbf{r}_1), & \varphi_{k_u}(\mathbf{r}_2) \\ \varphi_{k_v}(\mathbf{r}_1), & \varphi_{k_v}(\mathbf{r}_2) \end{matrix} \right| \eta_+(\sigma_1) \eta_+(\sigma_2) \Psi^{uv; 12} + \sum_{u < v}^{(-)} \left| \begin{matrix} \varphi_{k_u}(\mathbf{r}_1), & \varphi_{k_u}(\mathbf{r}_2) \\ \varphi_{k_v}(\mathbf{r}_1), & \varphi_{k_v}(\mathbf{r}_2) \end{matrix} \right| \eta_-(\sigma_1) \eta_-(\sigma_2) \times \right. \end{aligned}$$

$$\begin{aligned}
& \times \Psi_{uv; 12} + \sum_u^{(+)} \sum_v^{(-)} \left| \frac{\varphi_{k_u}(\mathbf{r}_1) \eta_+(\sigma_1), \varphi_{k_u}(\mathbf{r}_2) \eta_+(\sigma_2)}{\varphi_{k_v}(\mathbf{r}_1) \eta_-(\sigma_1), \varphi_{k_v}(\mathbf{r}_2) \eta_-(\sigma_2)} \right| \Psi_{uv; 12} = \frac{(N'-2)!}{N'!} \left\{ \left( \sum_{l < p}^{(+)} \sum_{u < v}^{(+)} + \right. \right. \\
& + \sum_{l < p}^{(-)} \sum_{u < v}^{(-)} \left. \right) \delta_{l,u} \delta_{p,v} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \left| \frac{\varphi_{k_l}^*(\mathbf{r}_1), \varphi_{k_l}^*(\mathbf{r}_2)}{\varphi_{k_p}^*(\mathbf{r}_1), \varphi_{k_p}^*(\mathbf{r}_2)} \right| \cdot \left| \frac{\varphi_{k_u}(\mathbf{r}_1), \varphi_{k_u}(\mathbf{r}_2)}{\varphi_{k_v}(\mathbf{r}_1), \varphi_{k_v}(\mathbf{r}_2)} \right| \frac{e^2}{r_{12}} \left( 1 - \right. \\
& - \left. \frac{2}{\pi} \int_0^{k_c r_{12}} d\tau \frac{\sin \tau}{\tau} \right) + \sum_{l,u}^{(+)} \sum_{p,v}^{(-)} \delta_{l,u} \delta_{p,v} \int d\mathbf{r}_1 \int d\mathbf{r}_2 [\varphi_{k_l}^*(\mathbf{r}_1) \varphi_{k_l}(\mathbf{r}_1) \varphi_{k_p}^*(\mathbf{r}_2) \varphi_{k_p}(\mathbf{r}_2) + \\
& + \varphi_{k_p}^*(\mathbf{r}_1) \varphi_{k_p}(\mathbf{r}_1) \varphi_{k_l}^*(\mathbf{r}_2) \varphi_{k_l}(\mathbf{r}_2)] \frac{e^2}{r_{12}} \left( 1 - \frac{2}{\pi} \int_0^{k_c r_{12}} d\tau \frac{\sin \tau}{\tau} \right) \left. \right\} \\
& = \frac{2}{N'(N'-1)} \left[ \frac{e^2}{V^2} \sum_{l < p} \iint \frac{d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r}_1 - \mathbf{r}_2|} d\tau \frac{\sin \tau}{\tau} \right) - \right. \\
& - \left. \frac{e^2}{V^2} \left( \sum_{l < p}^{(+)} + \sum_{l < p}^{(-)} \right) \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^{i(\mathbf{k}_p - \mathbf{k}_l) \cdot (\mathbf{r}_1 - \mathbf{r}_2)}}{|\mathbf{r}_1 - \mathbf{r}_2|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r}_1 - \mathbf{r}_2|} d\tau \frac{\sin \tau}{\tau} \right) \right]. \quad (3.33b)
\end{aligned}$$

In calculating (3.33b), we made use of the well-known fact that the spin functions are orthonormal,

$$\begin{aligned}
\sum_{\sigma} \eta_+^*(\sigma) \eta_+(\sigma) &= \sum_{\sigma} \eta_-^*(\sigma) \eta_-(\sigma) = 1, \\
\sum_{\sigma} \eta_+^*(\sigma) \eta_-(\sigma) &= \sum_{\sigma} \eta_-^*(\sigma) \eta_+(\sigma) = 0.
\end{aligned}$$

Since  $\sum_{l < p} = \frac{N'(N'-1)}{2}$ , we have, finally,

$$\begin{aligned}
& \left( \Psi^*, \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r}_1 - \mathbf{r}_2|} d\tau \frac{\sin \tau}{\tau} \right) \Psi \right) = \frac{e^2}{V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r} - \mathbf{r}'|} d\tau \frac{\sin \tau}{\tau} \right) - \\
& - \frac{2}{N'(N'-1)} \frac{e^2}{V^2} \left( \sum_{l < p}^{(+)} + \sum_{l < p}^{(-)} \right) \iint d\mathbf{r} d\mathbf{r}' \frac{e^{i(\mathbf{k}_p - \mathbf{k}_l) \cdot (\mathbf{r} - \mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r} - \mathbf{r}'|} d\tau \frac{\sin \tau}{\tau} \right) \quad (3.33c)
\end{aligned}$$

or,

$$\left( \Psi^*, \sum_{i < j} \frac{e^2}{r_{ij}} \left( 1 - \frac{2}{\pi} \int_0^{k_c r_{ij}} d\tau \frac{\sin \tau}{\tau} \right) \Psi \right)$$

$$\begin{aligned}
&= \frac{N'(N'-1)e^2}{2V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \left( 1 - \frac{2}{\pi} \int_0^{k_c|\mathbf{r}-\mathbf{r}'|} d\tau \frac{\sin \tau}{\tau} \right) - \\
&- \frac{e^2}{V^2} \left( \sum_{l < p}^{(+)} + \sum_{l < p}^{(-)} \right) \iint d\mathbf{r} d\mathbf{r}' \frac{e^{i(\mathbf{k}_p - \mathbf{k}_l) \cdot (\mathbf{r} - \mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|} \left( 1 - \frac{2}{\pi} \int_0^{k_c|\mathbf{r}-\mathbf{r}'|} d\tau \frac{\sin \tau}{\tau} \right). \quad (3.33d)
\end{aligned}$$

In the last term of eq. (3.33d) we make the substitution

$$\begin{aligned}
\mathbf{r} - \mathbf{r}' &= \vec{\varrho}, & \mathbf{r} &= \mathbf{R} + \frac{1}{2} \vec{\varrho}, & d\mathbf{r} d\mathbf{r}' &= d\vec{\varrho} d\mathbf{R}, \\
\mathbf{r} + \mathbf{r}' &= 2\mathbf{R}, & \mathbf{r}' &= \mathbf{R} - \frac{1}{2} \vec{\varrho},
\end{aligned}$$

and proceed to the limit  $N' \rightarrow +\infty, V \rightarrow +\infty, \frac{N'}{V} = \text{const}$ ,

$$\begin{aligned}
&\iint d\mathbf{r} d\mathbf{r}' \frac{e^{i(\mathbf{k}_p - \mathbf{k}_l) \cdot (\mathbf{r} - \mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|} \left( 1 - \frac{2}{\pi} \int_0^{k_c|\mathbf{r}-\mathbf{r}'|} d\tau \frac{\sin \tau}{\tau} \right) \\
&= \int d\vec{\varrho} \frac{e^{i(\mathbf{k}_p - \mathbf{k}_l) \cdot \vec{\varrho}}}{\varrho} \left( 1 - \frac{2}{\pi} \int_0^{k_c \varrho} d\tau \frac{\sin \tau}{\tau} \right) \int d\mathbf{R} \\
&= \frac{4\pi V}{|\mathbf{k}_p - \mathbf{k}_l|} \int_0^{+\infty} d\varrho \sin |\mathbf{k}_p - \mathbf{k}_l| \varrho \left( 1 - \frac{2}{\pi} \int_0^{k_c \varrho} d\tau \frac{\sin \tau}{\tau} \right) \\
&= \frac{4\pi V}{|\mathbf{k}_p - \mathbf{k}_l|} \left[ -\frac{1}{|\mathbf{k}_p - \mathbf{k}_l|} \cos |\mathbf{k}_p - \mathbf{k}_l| \varrho \left( 1 - \frac{2}{\pi} \int_0^{k_c \varrho} d\tau \frac{\sin \tau}{\tau} \right) \right]_0^{+\infty} - \\
&- \frac{2}{\pi |\mathbf{k}_p - \mathbf{k}_l|} \int_0^{+\infty} d\varrho \frac{\cos |\mathbf{k}_p - \mathbf{k}_l| \varrho \cdot \sin k_c \varrho}{\varrho} \Big] = \frac{4\pi V}{(\mathbf{k}_p - \mathbf{k}_l)^2} \left\{ 1 - \frac{1}{\pi} \times \right. \\
&\times \left. \int_0^{+\infty} \frac{d\varrho}{\varrho} [\sin(k_c + |\mathbf{k}_p - \mathbf{k}_l|) \varrho + \sin(k_c - |\mathbf{k}_p - \mathbf{k}_l|) \varrho] \right\} = \frac{4\pi V}{(\mathbf{k}_p - \mathbf{k}_l)^2}; |\mathbf{k}_p - \mathbf{k}_l| > k_c. \quad (3.33e)
\end{aligned}$$

If we now define  $q_0$  from (3.7) as

$$\frac{2\pi N' e^2}{mV} q_0^2 = \frac{N'(N'-1)e^2}{\pi V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \int_0^{k_c|\mathbf{r}-\mathbf{r}'|} d\tau \frac{\sin \tau}{\tau} = \frac{N'(N'-1)e^2}{\pi V} \int \frac{d\vec{\varrho}}{\varrho} \int_0^{k_c \varrho} d\tau \frac{\sin \tau}{\tau},$$

i.e.

$$q_0 = \left( \frac{(N'-1)m}{2\pi^2} \int \frac{d\vec{\varrho}}{\varrho} \int_0^{k_c \varrho} d\tau \frac{\sin \tau}{\tau} \right)^{1/2}, \quad (3.34)$$



then the first term in eq. (3.33d) cancels the last two terms in (3.8) and the expression  $\frac{2\pi N' e^2}{mV} q_0^2$ . The last elimination is due to (3.34). The proof is straightforward:

$$\begin{aligned} A &= \frac{N'(N'-1)e^2}{2V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} - \frac{N'e^2}{V} \sum_{i=1}^{N'} \int \frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{r}_i|} + \frac{N'^2 e^2}{2V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \\ &= \frac{N'^2 e^2}{V} \left( \frac{1}{2} + \frac{1}{2} - 1 \right) \int \frac{d\vec{\varrho}}{\varrho} - \frac{N'e^2}{2V} \int \frac{d\vec{\varrho}}{\varrho} = -\frac{N'e^2}{2V} \int \frac{d\vec{\varrho}}{\varrho}. \end{aligned}$$

Per one particle,

$$\frac{1}{N'} A = -\frac{e^2}{2V} \int \frac{d\vec{\varrho}}{\varrho} \rightarrow 0 \quad (3.35)$$

as  $V \rightarrow +\infty$ , since  $V$  increases to infinity as  $L^3$  ( $L$  — the cube edge), and the integral  $\int \frac{d\vec{\varrho}}{\varrho} = 4\pi \int d\varrho \cdot \varrho$  — as  $L^2$ .

We have yet to average the exchange integral of (3.33e) over the Fermi distribution obtaining, per one particle,

$$E_{\text{exch}} = -\frac{4\pi e^2}{N'V} \left( \sum_{\mathbf{k} < \mathbf{p}}^{(+)} + \sum_{\mathbf{k} < \mathbf{p}}^{(-)} \right) < \frac{1}{(\mathbf{k}_p - \mathbf{k}_l)^2} >, \quad (3.36)$$

wherein

$$< \frac{1}{(\mathbf{k}_p - \mathbf{k}_l)^2} > = \frac{\int d\mathbf{k}_p \int d\mathbf{k}_l (\mathbf{k}_p - \mathbf{k}_l)^{-2}}{\int d\mathbf{k}_p \int d\mathbf{k}_l}; \quad |\mathbf{k}_p - \mathbf{k}_l| > k_c, \quad k_c < k_F. \quad (3.37)$$

The mean value (3.37) was computed by Pines [9, 1953a] as

$$\begin{aligned} < \frac{1}{(\mathbf{k}_p - \mathbf{k}_l)^2} > &= \frac{9}{4} \frac{1}{k_F^3} \left[ 1 - \frac{4}{3} \frac{k_c}{k_F} + \frac{1}{2} \left( \frac{k_c}{k_F} \right)^2 - \frac{1}{48} \left( \frac{k_c}{k_F} \right)^4 \right] \\ &= \frac{9}{4} \frac{1}{k_0^3} \left( \frac{k_0}{k_F} \right)^2 \left[ 1 - \frac{4}{3} \beta \frac{k_0}{k_F} + \frac{1}{2} \beta^2 \left( \frac{k_0}{k_F} \right)^2 - \frac{1}{48} \beta^4 \left( \frac{k_0}{k_F} \right)^4 \right] \\ &= \frac{9}{4} \frac{1}{k_0^3} \left( 1 - \frac{\vartheta}{3} \beta^3 \right)^{-2/3} \left[ 1 - \frac{4\beta}{3 \left( 1 - \frac{\vartheta}{3} \beta^3 \right)^{1/3}} + \frac{\beta^2}{2 \left( 1 - \frac{\vartheta}{3} \beta^3 \right)^{2/3}} - \right. \\ &\quad \left. - \frac{\beta^4}{48 \left( 1 - \frac{\vartheta}{3} \beta^3 \right)^{4/3}} \right]. \end{aligned} \quad (3.38)$$

It is readily verified that

$$\sum_{\mathbf{k} < \mathbf{p}}^{(+)} + \sum_{\mathbf{k} < \mathbf{p}}^{(-)} = \frac{N'^2 \vartheta}{2}, \quad (3.39)$$

whence

$$E_{\text{exch}} = -\frac{9\pi N' \vartheta}{2Vk_0^3} \frac{e^2 k_0}{\left(1 - \frac{\vartheta}{3} \beta^3\right)^{2/3}} \left[ 1 - \frac{4\beta}{3 \left(1 - \frac{\vartheta}{3} \beta^3\right)^{1/3}} + \frac{\beta^2}{2 \left(1 - \frac{\vartheta}{3} \beta^3\right)^{2/3}} - \frac{\beta^4}{48 \left(1 - \frac{\vartheta}{3} \beta^3\right)^{1/3}} \right] = -\frac{3}{2\pi} \left( \frac{9\pi \vartheta}{2} \right)^{1/3} \frac{1}{r_s} \left[ \left(1 - \frac{\vartheta}{3} \beta^3\right)^{1/3} - \frac{4\beta}{3} + \frac{\beta^2}{2 \left(1 - \frac{\vartheta}{3} \beta^3\right)^{1/3}} - \frac{\beta^4}{48 \left(1 - \frac{\vartheta}{3} \beta^3\right)} \right] \text{ Ry.}$$

In the two magnetic cases

$$E_{\text{exch}}^{\uparrow\downarrow} = -\frac{0.9163}{r_s} \left[ \left(1 - \frac{1}{6} \beta^3\right)^{1/3} - \frac{4}{3} \beta + \frac{\beta^2}{2 \left(1 - \frac{1}{6} \beta^3\right)^{1/3}} - \frac{\beta^4}{48 \left(1 - \frac{1}{6} \beta^3\right)} \right] \text{ Ry,} \quad (3.40)$$

$$E_{\text{exch}}^{\uparrow\uparrow} = -\frac{1.1544}{r_s} \left[ \left(1 - \frac{1}{3} \beta^3\right)^{1/3} - \frac{4}{3} \beta + \frac{\beta^2}{2 \left(1 - \frac{1}{3} \beta^3\right)^{1/3}} - \frac{\beta^4}{48 \left(1 - \frac{1}{3} \beta^3\right)} \right] \text{ Ry.} \quad (3.41)$$

Assembling all results obtained (3.21), (3.29), (3.31), (3.40), and their parallel spin analogues, we have

$$E_{\uparrow\downarrow} = \frac{2.2100}{r_s^2} \left(1 - \frac{1}{6} \beta^2\right)^{2/3} + \frac{0.8661 \beta^3}{r_s^{3/2} \left(1 - \frac{1}{6} \beta^3\right)^{1/2}} - \frac{1.2217 \beta}{r_s} - \frac{0.9163}{r_s} \left[ \left(1 - \frac{1}{6} \beta^3\right)^{1/3} - \frac{4}{3} \beta + \frac{\beta^2}{2 \left(1 - \frac{1}{6} \beta^3\right)^{1/3}} - \frac{\beta^4}{48 \left(1 - \frac{1}{6} \beta^3\right)} \right] \text{ Ry,} \quad (3.42)$$

$$E_{\uparrow\uparrow} = \frac{3.5077}{r_s^2} \left(1 - \frac{1}{3} \beta^3\right)^{2/3} + \frac{1.7321 \beta^3}{r_s^{3/2} \left(1 - \frac{1}{3} \beta^3\right)^{1/2}} - \frac{1.5392 \beta}{r_s} - \frac{1.1544}{r_s} \left[ \left(1 - \frac{1}{3} \beta^3\right)^{1/3} - \frac{4}{3} \beta + \frac{\beta^2}{2 \left(1 - \frac{1}{3} \beta^3\right)^{1/3}} - \frac{\beta^4}{48 \left(1 - \frac{1}{3} \beta^3\right)} \right] \text{ Ry.} \quad (3.43)$$

The relations (3.42) and (3.43) must now be minimalized with respect to  $\beta$ , hence

$$\frac{\partial E_{\uparrow\downarrow}}{\partial \beta} = -\frac{0.9163 \beta}{r_s \left(1 - \frac{1}{6} \beta^3\right)^{1/3}} + \left[ \frac{2.5982}{r_s^{3/2} \left(1 - \frac{1}{6} \beta^3\right)^{1/2}} + \frac{0.1527}{r_s \left(1 - \frac{1}{6} \beta^3\right)^{2/3}} - \frac{0.7367}{r_s^2 \left(1 - \frac{1}{6} \beta^3\right)^{1/3}} \right] \beta^2 + \frac{0.0764 \beta^3}{r_s \left(1 - \frac{1}{6} \beta^3\right)} - \frac{0.0764 \beta^4}{r_s \left(1 - \frac{1}{6} \beta^3\right)^{1/3}} + \frac{0.2165 \beta^5}{r_s^{1/2} \left(1 - \frac{1}{6} \beta^3\right)^{1/2}} + \frac{0.0095 \beta^6}{r_s \left(1 - \frac{1}{6} \beta^3\right)^2} = 0, \quad (3.44)$$

$$\frac{\partial E_{\uparrow\uparrow}}{\partial \beta} = -\frac{1.1544 \beta}{r_s(1 - \frac{1}{3}\beta^3)^{1/3}} + \left[ \frac{3.4642}{r_s^{3/2}(1 - \frac{1}{3}\beta^3)^{1/2}} - \frac{0.3848}{r_s(1 - \frac{1}{3}\beta^3)^{2/3}} - \frac{2.3385}{r_s^2(1 - \frac{1}{3}\beta^3)^{1/2}} \right] \beta^2 + \frac{0.0962 \beta^3}{r_s(1 - \frac{1}{3}\beta^3)} - \frac{0.1924 \beta^4}{r_s(1 - \frac{1}{3}\beta^3)^{1/2}} + \frac{0.8661 \beta^5}{r_s^{3/2}(1 - \frac{1}{3}\beta^3)^{1/2}} + \frac{0.0241 \beta^6}{r_s(1 - \frac{1}{3}\beta^3)} = 0. \quad (3.45)$$

We compute the correlation energy for the non-magnetic state only, since the energy of the magnetic state lies higher and therefore this state is not realized. We define the correlation energy as

$$E_{\text{corr}} = E_{\uparrow\uparrow} - E, \quad (3.46)$$

$$E = \frac{2.2100}{r_s^2} - \frac{0.9163}{r_s}. \quad (3.47)$$

In Table I, the above listed quantities are compared for some alkali metals.

Table I

Metal			Li	Na	K	Rb	Cs
$r_s$	1	2	3.22*	3.96*	4.87*	5.18*	5.57*
$\beta_{\min}^{\uparrow\downarrow}$	0.4450	0.5466	0.6380	0.6820	0.7305	0.7454	0.7625
$\beta_{\min}^{\uparrow\uparrow}$	—	—	0.6536	0.6753	0.6994	0.7065	0.7226
$E_{\uparrow\downarrow}$ Ry	1.2629	0.0710	-0.0915	-0.1092	-0.1126	-0.1117	-0.1103
$E$ Ry	1.2937	0.0943	-0.0715	-0.0905	-0.0950	-0.0945	-0.0933
$E_{\uparrow\uparrow}$ Ry	—	—	-0.0198	-0.0689	-0.0918	-0.0951	-0.0970
$E_{\text{corr}}$ Ry	-0.0303	-0.0233	-0.0200	-0.0187	-0.0176	-0.0172	-0.0170
$E_{\text{corr}}^*$ Ry	—	—	-0.240	-0.269	-0.308	-0.319	-0.333

The correlation energy is approximated to  $\sim 13\%$  accuracy by the following formula:

$$E_{\text{corr}} = -0.0502 + 0.0622 \ln r_s - 0.0132 \cdot r_s \text{ Ry}, \quad 3 \leq r_s \leq 6. \quad (3.48)$$

The corresponding quantity obtained by Pines [9, 1958c] is

$$E_{\text{corr}} = -0.140 + 0.0622 \ln r_s - 0.0038 \cdot r_s \text{ Ry} \quad \text{for all } r_s, \quad (3.49)$$

while Gell-Mann and Brueckner (1957) give

$$E_{\text{corr}} = -0.096 + 0.0622 \ln r_s + O(r_s) \text{ Ry}, \quad r_s \ll 1. \quad (3.50)$$

Here  $O(r_s)$  includes all terms  $r_s^n$  and  $r_s^n \ln r_s$  from  $n = 1$  onwards.

Figs. 1 and 2 illustrate the data of the Table I.

In the region  $r_s \leq 1$  inclusive of the high density region  $r_s \ll 1$  the foregoing calculation does not apply. This may be seen from (3.44) and (3.45), where the coeffi-

\* The values marked with an asterisk have been taken from Pines' paper (1953a).



cient of  $\beta^2$  points to anomalous behaviour just in this interval. The physical reason for this anomaly is clear; namely, we used the ground state function in the form of (3.9), whereas in the high density region this form is no longer adequate for describing

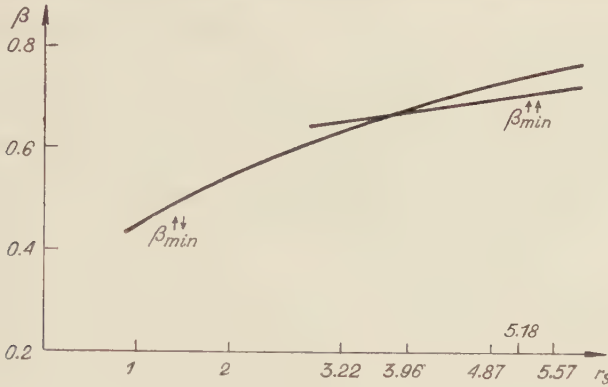


Fig. 1

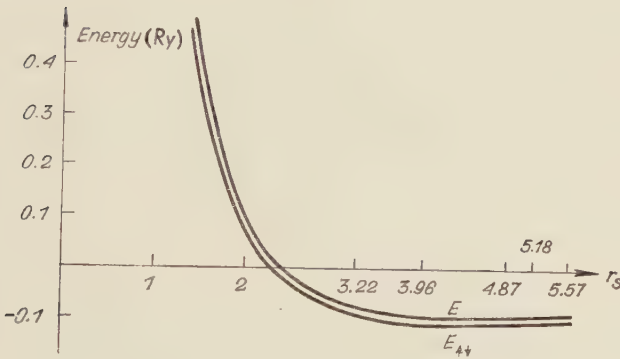


Fig. 2

the system. Therefore it becomes necessary to apply perturbation technique either in order to improve the state function (3.9), or, and this is what the present author prefers to do, to eliminate in some approximation the interaction term in the Hamiltonian (3.8). This latter procedure will be followed in a subsequent paper.

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## COLLECTIVE OSCILLATIONS IN AN ELECTRON GAS OF METALLIC DENSITY. THE CORRELATION ENERGY. II

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In order to isolate the plasmons in the Hamiltonian derived in the first part of the present paper, the canonical transformation to independent plasmon modes is applied. The formula for the correlation energy obtained is nearly the same as that of the Gell-Mann and Brueckner high density electron gas theory. The absolute value of the constant in the correlation energy is by 4 % larger than in the Gell-Mann and Brueckner approach.

The second order energy shift within the Rayleigh-Schroedinger perturbation theory framework is evaluated.

*1. Introduction*

In the first part of the present paper we proposed a new formulation of the collective description without subsidiary conditions. Thereafter we evaluated the correlation energy of the electron gas system.

In the present part we proceed to transform the Hamiltonian (I 3.8). The aim of this procedure is to uncouple the individual electrons from the plasmons. Subsequently we apply the standart method to obtain the ground state energy and the correlation energy.

In order to obtain the second order energy correction in section 4, the Rayleigh-Schroedinger perturbation theory is applied. Moreover the divergence types of the second order energy shifts are proved to differ from those computed by Brueckner (1958).

Quite recently, the Green function method of Schwinger (1951) and of Gell-Mann and Low (1951), has been successfully applied to problems of quantum mechanics Hubbard (1957b), (1958c), Galitskiĭ and Migdal (1958), Klein and Prange (1958), Kanazawa and Watabe (1960), Kanazawa, Misawa and Fujita (1960).

The problem of the Green function method in application to an electron gas of metallic density will be dealt with in a subsequent independent paper.

## 2. The canonical transformation to independent collective modes

The notation throughout the present part is the same as in part I hence no explanation will be given here.

The Hamiltonian of the system, as derived in part I of this paper (I 3.8), is

$$\begin{aligned}
 \hat{H} = & \sum_{i=1}^{N'} \frac{\hat{p}_i^2}{2m} + \frac{2\pi}{V} \sum_{|\mathbf{k}| > k_c} \frac{q_k q_{-k} - N' e^2}{k^2} + \\
 & + \frac{e}{m} \sqrt{\frac{4\pi}{V}} \sum_{i=1}^{N'} \sum_{|\mathbf{k}| \leq k_c} q_k \vec{\varepsilon}_k \cdot (\hat{\mathbf{p}}_i - \hbar \mathbf{k}/2) e^{i\mathbf{k} \cdot \mathbf{r}_i} - \\
 & - \frac{1}{2} \sum'_{|\mathbf{k}| \leq k_c} (p_k p_{-k} + \omega_p^2 q_k q_{-k}) - \frac{2\pi e^2}{mV} \sum_{i=1}^{N'} \sum'_{\substack{|\mathbf{k}| \leq k_c \\ |\mathbf{k}'| \leq k_c \\ \mathbf{k} + \mathbf{k}' \neq 0}} q_k q_{k'} \vec{\varepsilon}_k \cdot \vec{\varepsilon}_{k'} e^{i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}_i} + \\
 & + \frac{2\pi e^2}{mV} q_0 \sum_{i=1}^{N'} \sum'_{|\mathbf{k}| \leq k_c} q_k \mathbf{z}^0 \cdot \vec{\varepsilon}_k e^{i\mathbf{k} \cdot \mathbf{r}_i} + \frac{2\pi N' e^2}{mV} q_0^2 - \frac{2\pi N' e^2}{V} \sum_{|\mathbf{k}| \leq k_c} \frac{1}{k^2} - \\
 & - \frac{N'^2 e^2}{V} \int \frac{d\mathbf{r}}{r} + \frac{N'^2 e^2}{2V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad \omega_p^2 = \frac{4\pi N' e^2}{mV}. \quad (2.1)
 \end{aligned}$$

The frequency of plasma oscillations  $\omega_p$  is, of course, not the same as in Bohm and Pines' paper (1953b), since here the number of individual electrons is smaller. Denoting the Langmuir frequency by  $\omega_L$ , we have

$$\omega_p^2 = \frac{4\pi N e^2}{mV} \frac{N'}{N} = \omega_L^2 \left(1 - \frac{\vartheta}{3} \beta^3\right), \quad (2.2)$$

wherein

$$\omega_L^2 = \frac{4\pi N e^2}{mV} \quad (2.3)$$

and  $\vartheta$  and  $\beta$  are given by eqs. (I 3.11) and (I 3.15), respectively. Thus, a certain shift due to excitation of electron-hole pairs is seen to occur in the plasma frequency  $\omega_L$ .

Our main task now consists in transforming the Hamiltonian (2.1), so as to eliminate the interaction term

$$\hat{H}_{\text{inter}} = \frac{e}{m} \sqrt{\frac{4\pi}{V}} \sum_{i=1}^{N'} \sum'_{|\mathbf{k}| \leq k_c} q_k \vec{\varepsilon}_k \cdot (\hat{\mathbf{p}}_i - \hbar \mathbf{k}/2) e^{i\mathbf{k} \cdot \mathbf{r}_i}. \quad (2.4)$$

The perturbation-theoretic treatment of this problem is due to Bohm and Pines



(1953b). The generating function of the transformation is known to be of the form

$$\hat{S} = -i \frac{e\hbar}{m} \sum_{i=1}^{N'} \sum'_{|\mathbf{k}| \leq k_c} h_k \cdot \mathbf{k} \left[ \frac{\vec{\epsilon}_k \cdot (\hat{\mathbf{p}}_i - \hbar \mathbf{k}/2)}{\omega_k - \mathbf{k} \cdot \hat{\mathbf{p}}_i/m + \hbar k^2/2m} e^{i\mathbf{k} \cdot \mathbf{r}_i} a_k - a_k^* e^{-i\mathbf{k} \cdot \mathbf{r}_i} \frac{\vec{\epsilon}_k \cdot (\hat{\mathbf{p}}_i - \hbar \mathbf{k}/2)}{\omega_k - \mathbf{k} \cdot \hat{\mathbf{p}}_i/m + \hbar k^2/2m} \right], \quad h_k = \sqrt{\frac{2\pi}{V \hbar \omega_k \cdot k^2}}. \quad (2.5)$$

We transform the Hamiltonian (2.1) as follows:

$$\hat{H}_{\text{new}} = e^{-i\hat{S}/\hbar} \hat{H} e^{i\hat{S}/\hbar}. \quad (2.6)$$

$\omega_k$  is the dispersion frequency satisfying the relation

$$1 = \frac{4\pi e^2}{mV} \sum_{i=1}^{N'} \frac{1}{(\omega_k - \mathbf{k} \cdot \hat{\mathbf{p}}_i/m)^2 - \hbar^2 k^2/4m^2} \quad (2.7)$$

or

$$\omega_k = \omega_p \left( 1 + \frac{k^2}{2N' m^2 \omega_p^2} \sum_{i=1}^{N'} \hat{\mathbf{p}}_i^2 + \frac{\hbar^2 k^4}{8m^2 \omega_p^2} + \dots \right). \quad (2.8)$$

The right hand side of eq. (2.6) may be expanded in a  $\hat{H}, \hat{S}$  commutator series. Each  $n$ -fold commutator

$$[\hat{H}, \hat{S}]_n = [\dots [[[\hat{H}, \hat{S}], 1^2 \hat{S}], 1^3 \hat{S}] \dots, 1^n \hat{S}] \quad (2.9)$$

is proportional to the operator  $(\mathbf{k} \cdot \hat{\mathbf{p}}_i/m\omega_k)^n$ . The mean of the operator  $(\mathbf{k} \cdot \hat{\mathbf{p}}_i/m\omega_k)^2$

$$g^2 = \langle (\mathbf{k} \cdot \hat{\mathbf{p}}_i/m\omega_k)^2 \rangle \approx \langle (\mathbf{k} \cdot \hat{\mathbf{p}}_i/m\omega_p)^2 \rangle = 0.5426 \frac{\alpha^2}{\left(1 + \frac{\vartheta}{3} \alpha^3\right)^{1/3}} \frac{1}{r_s}, \quad (2.10)$$

$$\alpha = k_c/k_F \quad (2.11)$$

will be termed the coupling constant for the electron-plasmon interaction.

Applying the random phase approximation (Bohm and Pines 1952a)), and the canonical transformation with the generating function (2.5), we obtain

$$\begin{aligned} \hat{H}_{\text{new}} = & \sum_{i=1}^{N'} \frac{\hat{p}_i^2}{2m^*} + e^2 \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r}_i - \mathbf{r}_j|} d\tau \frac{\sin \tau}{\tau} \right) + \\ & + \sum_{|\mathbf{k}| \leq k_c} \hbar \omega_k \left( a_k^* a_k + \frac{1}{2} \right) - \frac{2\pi N' e^2}{V} \sum_{|\mathbf{k}| \leq k_c} \frac{1}{k^2} + \frac{2\pi N' e^2}{mV} q_0^2 - \\ & - \frac{N'^2 e^2}{V} \int \frac{d\mathbf{r}}{r} + \frac{N'^2 e^2}{2V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad \hat{H}_{\text{new}} \Psi = E \Psi, \end{aligned} \quad (2.12)$$

wherein the effective mass  $m^*$  is given by

$$\frac{m}{m^*} = \left( 1 - \frac{V}{N'} \frac{k_c^3}{3 \cdot 3! \pi^2} \right) = \left( 1 - \frac{\vartheta}{3} \alpha^3 \right). \quad (2.13)$$

A detailed derivation of eq. (2.12) is to be found in the paper by Bohm and Pines (1953b).

Since we investigate the ground state of the system only, we can transform the oscillator part of the Hamiltonian (2.12). Using the plasmon part of the wave function (I 3.9), we have

$$\langle \hat{H}_{\text{osc}} \rangle = \Phi_0^* \sum_{|\mathbf{k}| \leq k_c} \hbar \omega_k (a_k^* a_k + 1/2) \Phi_0 = \frac{1}{2} \sum_{|\mathbf{k}| \leq k_c} \hbar \omega_k$$

or, with respect to eq. (2.8),

$$\begin{aligned} \langle \hat{H}_{\text{osc}} \rangle &= \frac{\hbar \omega_p}{2} \sum_{|\mathbf{k}| \leq k_c} \left( 1 + \frac{k^2}{N' m \omega_p^2} \sum_{i=1}^{N'} \frac{\hat{p}_i^2}{2m} + \frac{\hbar^2 k^4}{8m^2 \omega_p^2} \right) = \frac{\hbar \omega_p}{2} \left[ \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_c} d\mathbf{k} + \right. \\ &\quad \left. + \frac{1}{N' m \omega_p^2} \sum_{i=1}^{N'} \frac{\hat{p}_i^2}{2m} \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_c} d\mathbf{k} \cdot k^2 + \frac{\hbar^2}{8m^2 \omega_p^2} \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| \leq k_c} d\mathbf{k} \cdot k^4 \right] \\ &= \frac{\hbar \omega_p}{2} \left[ \frac{V}{8\pi^3} \frac{4\pi}{3} k_c^3 + \frac{1}{N' m \omega_p^2} \sum_{i=1}^{N'} \frac{\hat{p}_i^2}{2m} \frac{V}{8\pi^3} \frac{4\pi}{5} k_c^5 + \frac{\hbar^2}{8m^2 \omega_p^2} \frac{V}{8\pi^3} \frac{4\pi}{7} k_c^7 \right] \\ &= \left[ \frac{\hbar \omega_p}{2} \vartheta N' \alpha^3 + \frac{\sqrt{3}}{10} \vartheta \left( \frac{9\pi \vartheta}{2} \right)^{3/2} \frac{\alpha^5}{\left( 1 + \frac{\vartheta}{3} \alpha^3 \right)^{1/6}} \frac{1}{r_s^{1/2}} \sum_{i=1}^{N'} \frac{\hat{p}_i^2}{2m} + \right. \\ &\quad \left. \frac{\sqrt{3} \vartheta}{56} N' \left( \frac{9\pi \vartheta}{2} \right)^{3/2} \frac{\alpha^7}{\left( 1 + \frac{\vartheta}{3} \alpha^3 \right)^{1/6}} \frac{1}{r_s^{3/2}} \frac{e^2}{2a_0} \right]. \quad (2.14) \end{aligned}$$

We may now delete the fifth, sixth and seventh terms in eq. (2.12) as they only serve to cancel the Coulomb integral of the second term. By eq. (2.14), we have

$$\hat{\mathcal{H}} = \sum_{i=1}^{N'} \frac{\hat{p}_i^2}{2m^{**}} + e^2 \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r}_i - \mathbf{r}_j|} d\tau \frac{\sin \tau}{\tau} \right),$$

$$\hat{\mathcal{H}} \Psi = E' \Psi, \quad (2.15)$$

wherein

$$\frac{m}{m^{**}} = \left[ 1 - \frac{\vartheta}{3} \alpha^3 + \frac{\sqrt{3}}{10} \vartheta \left( \frac{9\pi \vartheta}{2} \right)^{3/2} \frac{\alpha^5}{\left( 1 + \frac{\vartheta}{3} \alpha^3 \right)^{1/6}} \frac{1}{r_s^{1/2}} \right] \quad (2.16)$$

and

$$E' = E + N' \left[ \frac{2}{\pi} \left( \frac{9\pi\vartheta}{2} \right)^{1/2} \frac{\alpha}{\left( 1 + \frac{\vartheta}{3} \alpha^3 \right)^{1/2}} \frac{1}{r_s} - \sqrt{3} \vartheta \frac{\alpha^3}{\left( 1 + \frac{\vartheta}{3} \alpha^3 \right)^{1/2}} \frac{1}{r_s^{3/2}} - \frac{\sqrt{3}}{56} \vartheta \left( \frac{9\pi\vartheta}{2} \right)^{1/2} \frac{\alpha^7}{\left( 1 + \frac{\vartheta}{3} \alpha^3 \right)^{5/2}} \frac{1}{r_s^{1/2}} \right] \text{Ry.} \quad (2.17)$$

We have transferred one part of the long-range Coulomb energy (2.14) to the kinetic energy of the individual electrons. This step implies the dependence of the effective mass on the spacing parameter  $r_s$  as in eq. (2.16).

### 3. The correlation energy

All successive computations are the same as in part I; hence, we restrict ourselves to given the final result for the non-magnetic state only:

$$E_{\text{t4}} = \left\{ \frac{2.2099}{r_s^2} \left[ \frac{1 - \frac{1}{6} \alpha^3}{\left( 1 + \frac{1}{6} \alpha^3 \right)^{1/2}} + \frac{0.3190 \cdot \alpha^5}{r_s^{1/2} \left( 1 + \frac{1}{6} \alpha^3 \right)^{5/2}} \right] - \frac{0.9163}{r_s} \frac{1}{\left( 1 + \frac{1}{6} \alpha^3 \right)^{1/2}} \times \right. \\ \times \left[ 1 - \frac{4}{3} \alpha + \frac{1}{2} \alpha^2 - \frac{1}{48} \alpha^4 \right] - \frac{1.2217}{r_s} \frac{\alpha}{\left( 1 + \frac{1}{6} \alpha^3 \right)^{1/2}} + \frac{0.8661}{r_s^{3/2}} \frac{\alpha^3}{\left( 1 + \frac{1}{6} \alpha^3 \right)^{1/2}} + \\ \left. + \frac{0.2098 \cdot \alpha^7}{r_s^{5/2} \left( 1 + \frac{1}{6} \alpha^3 \right)^{5/2}} \right\} \text{Ry.} \quad (3.1)$$

The first term in eq. (3.1) represents the mean kinetic energy per one particle, the second — the exchange energy of short-range interactions, the third — the self-energy of long-range interactions, the fourth — the Coulomb long-range energy and the fifth — the correction due to dispersion of the oscillation frequency. Here, the designation “kinetic” energy is employed in a somewhat formal manner, since the first term in eq. (3.1) includes, in addition to the pure kinetic energy, certain interactions, such as i.a. a part of the Coulomb long-range energy. One part of the exchange energy (the second term in square brackets) cancels the long-range self-energy (the third term in eq. (3.1)).

We now proceed to minimize eq. (3.1) with respect to  $\alpha$ . The corresponding values of  $\alpha$  are computed numerically for  $r_s = 1, 2, 3, 4, 5, 6$ , Table 1. The remaining points for alkali metals are computed from the interpolation curve

$$\alpha = a_1 + a_2 \cdot r_s + a_3 \cdot r_s^2 + a_4 \cdot r_s^3 + a_5 \cdot r_s^4 + a_6 \cdot r_s^5. \quad (3.2)$$

Quite similarly the correlation energy

$$E_{\text{corr}}^{\text{t4}} = E_{\text{t4}} - E, \quad (3.3)$$

$$E = \frac{2.2099}{r_s^2} - \frac{0.9163}{r_s} \text{Ry,} \quad (3.4)$$

is evaluated for  $r_s = 1, 2, 3, 4, 5, 6$  directly (numerically), whereas, for the alkali metals, it has been obtained from the interpolation curve

$$E_{\text{corr}}^{+4} = b_1 + 0.0622 \ln r_s + b_2 \cdot r_s + b_3 \cdot r_s^2 + b_4 \cdot r_s^3 + b_5 \cdot r_s^4 + b_6 \cdot r_s^5. \tag{3.5}$$

Putting by turns  $r_s = 1, 2, 3, 4, 5, 6$  in eq. (3.5) and denoting the corresponding values of  $\alpha$  and  $E_{\text{corr}}^{+4}$  by  $\alpha^{(i)}$  and  $E_{+4}^{(i)}$ , respectively, we get, after some amount of algebra,

$$\begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 2 & 2^2 & 2^3 & 2^4 & 2^5 \\ 1 & 3 & 3^2 & 3^3 & 3^4 & 3^5 \\ 1 & 4 & 4^2 & 4^3 & 4^4 & 4^5 \\ 1 & 5 & 5^2 & 5^3 & 5^4 & 5^5 \\ 1 & 6 & 6^2 & 6^3 & 6^4 & 6^5 \end{pmatrix} \cdot \begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6 \end{pmatrix} = \begin{pmatrix} \varepsilon_{+4}^{(1)} \\ \varepsilon_{+4}^{(2)} \\ \varepsilon_{+4}^{(3)} \\ \varepsilon_{+4}^{(4)} \\ \varepsilon_{+4}^{(5)} \\ \varepsilon_{+4}^{(6)} \end{pmatrix} = \begin{pmatrix} E_{+4}^{(1)} \\ E_{+4}^{(2)} - 0.0431 \\ E_{+4}^{(3)} - 0.0683 \\ E_{+4}^{(4)} - 0.0862 \\ E_{+4}^{(5)} - 0.1001 \\ E_{+4}^{(6)} - 0.1114 \end{pmatrix}. \tag{3.6}$$

$$\left\{ \frac{\Delta_{ik}}{\Delta} \right\} = \begin{pmatrix} 6 & -\frac{87}{10} & \frac{29}{6} & -\frac{31}{24} & \frac{1}{6} & -\frac{1}{5!} \\ -15 & \frac{117}{4} & -\frac{461}{24} & \frac{137}{24} & -\frac{19}{24} & \frac{1}{4!} \\ 20 & -\frac{127}{3} & 31 & -\frac{121}{12} & \frac{3}{2} & -\frac{1}{12} \\ -15 & 33 & -\frac{307}{12} & \frac{107}{12} & -\frac{17}{12} & \frac{1}{12} \\ 6 & -\frac{27}{2} & \frac{65}{6} & -\frac{95}{24} & \frac{2}{3} & -\frac{1}{4!} \\ -1 & \frac{137}{60} & -\frac{15}{8} & \frac{17}{24} & -\frac{1}{8} & \frac{1}{5!} \end{pmatrix}, \tag{3.7}$$

wherein  $\Delta$  is the determinant of the square matrix in eq. (3.6) and  $\Delta^{ik}$  — its minor ( $i$  and  $k$  stand for the lines and columns to be deleted in the determinant  $\Delta$ ).

Numerical computation yields:

Table I

$r_s$	1	2	3	4	5	6
$\alpha$	0.4887	0.5748	0.6454	0.7034	0.7527	0.7975
$E_{+4}$ Ry	1.2339	0.0622	-0.0856	-0.1133	-0.1151	-0.1097
$E$ Ry	1.2936	0.0943	-0.0599	-0.0910	-0.0949	-0.0913
$E_{\text{corr}}^{+4}$ Ry	-0.0597	-0.0321	-0.0257	-0.0223	-0.0202	-0.0184



Since

$$a_j = \sum_{i=1}^6 \alpha^{(i)} \frac{\Delta^{ij}}{\Delta}, \quad (3.8)$$

$$b_j = \sum_{i=1}^6 \varepsilon_{\uparrow i}^{(i)} \frac{\Delta^{ij}}{\Delta}, \quad (3.9)$$

we may now make use of the values in Table I, obtaining

$$\alpha = 0.3859 + \frac{1}{6} 0.66591 \cdot r_s + \frac{1}{24} (-0.1891 \cdot r_s^2 - 0.0103 \cdot r_s^3 + 0.0031 \cdot r_s^4) - \\ - \frac{1}{120} 0.0007 \cdot r_s^5, \quad 1 \leq r_s \leq 6, \quad (3.10)$$

$$E_{\text{corr}}^{\uparrow\downarrow} = -0.0747 + 0.0622 \ln r_s + \frac{1}{3} (0.13889 \cdot r_s - 0.1265 \cdot r_s^2 + 0.0374 \cdot r_s^3 - \\ - 0.00505 \cdot r_s^4 + 0.00026 \cdot r_s^5) \text{ Ry}, \quad 1 \leq r_s \leq 6. \quad (3.11)$$

From (3.11) and (I 3.54) the constant in the correlation energy eq. (3.11), is seen to be by approximately 20% larger than that computed by Gell-Mann and Brueckner (1957).

Table II lists the interpolated values for the correlation energy eq. (3.11) for some alkali metals.

Table II

Metal	Li	Na	K	Rb	Cs
$r_s$	3,22	3,96	4,87	5,18	5,57
$\alpha$	0,6591	0,7013	0,7466	0,7610	0,7785
$E_{\uparrow\downarrow}^{\text{Ry}}$	-0,0956	-0,1128	-0,1153	-0,1142	-0,1124
$E^{\text{Ry}}$	-0,0715	-0,0905	-0,0950	-0,0945	-0,0933
$E_{\text{corr}}^{\uparrow\downarrow} \text{ Ry}$	-0,0241	-0,0223	-0,0203	-0,0197	-0,0191

The values of the correlation energy, as evaluated either with the help of eq. (3.10) or by eq. (3.11), are consistent within 3%.

#### 4. Second order correction to the correlation energy

Let us now investigate the magnitude of the second order energy shift. For this purpose we utilize the Rayleigh-Schroedinger perturbation theory (Brueckner (1958)) and the wave equation

$$\hat{\mathcal{H}}_0 \Psi = E_0 \Psi, \quad (4.1)$$

$$\hat{\mathcal{H}}_0 = \sum_{i=1}^{N'} \frac{\hat{p}_i^2}{2m^{**}}, \quad E_0 = \sum_{s=1}^{N'} \frac{\hbar^2 k_s^2}{2m^{**}}, \quad (4.2)$$

with the wave function  $\Psi$  given by (I 3.9). According to eq. (2.15) the Coulomb short-range interaction energy is of the form

$$h = \sum_{i < j} h_{ij}, \quad h_{ij} = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \left( 1 - \frac{2}{\pi} \int_0^{k_c |\mathbf{r}_i - \mathbf{r}_j|} d\tau \frac{\sin \tau}{\tau} \right) = \frac{4\pi e^2}{V} \sum_{|\mathbf{k}| > k_c} \frac{e^{i\mathbf{k} \cdot \mathbf{r}_{ij}}}{k^2}, \quad (4.3)$$

whence we obtain the following energy correction:

$$\varepsilon_2 = \left( \Psi^*, h \frac{1}{\hat{b}} h \Psi \right) = \left\langle h \frac{1}{\hat{b}} h \right\rangle, \quad (4.4)$$

with

$$\frac{1}{\hat{b}} = \frac{1 - \hat{P}_0}{E_0 - \hat{\mathcal{H}}_0}, \quad \hat{P}_0 \Phi = \begin{cases} \Phi & \text{when } \Phi = \Psi, \\ 0 & \text{otherwise.} \end{cases} \quad (4.5)$$

$\hat{P}_0$  is the projection operator on the unperturbed state  $\Psi$ . By (4.3) and (4.4), we have

$$\begin{aligned} \varepsilon_2 &= \sum_{\substack{i < j \\ i' < j'}} \left\langle h_{ij} \frac{1}{\hat{b}} h_{i'j'} \right\rangle = \sum_{i < j} \left\langle h_{ij} \frac{1}{\hat{b}} h_{ij} \right\rangle + \sum_{i < j < l} \left( \left\langle h_{jl} \frac{1}{\hat{b}} h_{ij} \right\rangle + \right. \\ &\quad + \left\langle h_{jl} \frac{1}{\hat{b}} h_{il} \right\rangle + \left\langle h_{il} \frac{1}{\hat{b}} h_{ij} \right\rangle + \left\langle h_{ij} \frac{1}{\hat{b}} h_{il} \right\rangle + \left\langle h_{ij} \frac{1}{\hat{b}} h_{jl} \right\rangle + \\ &\quad + \left. \left\langle h_{il} \frac{1}{\hat{b}} h_{jl} \right\rangle \right) + \sum_{i < j < l < p} \left( \left\langle h_{lp} \frac{1}{\hat{b}} h_{ij} \right\rangle + \left\langle h_{jp} \frac{1}{\hat{b}} h_{il} \right\rangle + \left\langle h_{jl} \frac{1}{\hat{b}} h_{ip} \right\rangle + \right. \\ &\quad + \left. \left\langle h_{ij} \frac{1}{\hat{b}} h_{lp} \right\rangle + \left\langle h_{il} \frac{1}{\hat{b}} h_{jp} \right\rangle + \left\langle h_{ip} \frac{1}{\hat{b}} h_{jl} \right\rangle \right). \end{aligned} \quad (4.6)$$

In Gell-Mann and Brueckner's paper (1957) all terms in the second and third sum vanish, since both authors put

$$\Phi = \prod_{i=1}^N \varphi_{k_i}(\mathbf{r}_i), \quad \varphi_k(\mathbf{r}) = \frac{1}{V^{1/2}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (4.7)$$

It is manifest that the wave function in the form of eq. (4.7) does not obey the Pauli principle. Thus, in their theory, the correlation effects due to the Pauli principle are neglected. In the present author's computation, the aforementioned terms are non-zero; albeit the evaluation of these terms is excessively tedious, and they will be omitted in the present paper. This yields

$$\varepsilon_2 = \sum_{i < j} \left( \Psi^*, h_{ij} \frac{1}{\hat{b}} h_{ij} \Psi \right) = \left( \frac{4\pi e^2}{V} \right)^2 \sum_{i < j} \sum_{\substack{|\mathbf{k}| > k_c \\ |\mathbf{k}'| > k_c}} \frac{1}{k^2 \cdot k'^2} \left( \Psi^*, e^{i\mathbf{k}' \cdot \mathbf{r}_{ij}} \frac{1}{\hat{b}} e^{i\mathbf{k} \cdot \mathbf{r}_{ij}} \Psi \right). \quad (4.8)$$

Let us compute the expression

$$A = \left( \Psi^*, e^{i\mathbf{k}' \cdot \mathbf{r}_{12}} \frac{1 - \hat{P}_0}{E_0 - \hat{\mathcal{H}}_0} e^{i\mathbf{k} \cdot \mathbf{r}_{12}} \Psi \right). \quad (4.9a)$$

Insertion of eq. (I 3.9) into eq. (4.9a) gives

$$\begin{aligned}
A &= \frac{1}{N'!} \sum_{\sigma_1, \dots, \sigma_{N'}} \int d\mathbf{r}_1 \dots \int d\mathbf{r}_{N'} \left[ \sum_{l < p}^{(+)} \left| \frac{\varphi_{k_l}^*(\mathbf{r}_1), \varphi_{k_l}^*(\mathbf{r}_2)}{\varphi_{k_p}^*(\mathbf{r}_1), \varphi_{k_p}^*(\mathbf{r}_2)} \right| \eta_+^*(\sigma_1) \eta_+^*(\sigma_2) \Psi^{*lp;12} + \right. \\
&\quad \left. + \sum_{l < p}^{(-)} \left| \frac{\varphi_{k_l}^*(\mathbf{r}_1), \varphi_{k_l}^*(\mathbf{r}_2)}{\varphi_{k_p}^*(\mathbf{r}_1), \varphi_{k_p}^*(\mathbf{r}_2)} \right| \eta_-^*(\sigma_1) \eta_-^*(\sigma_2) \Psi^{*lp;12} + \right. \\
&\quad \left. + \sum_l^{(+)} \sum_p^{(-)} \left| \frac{\varphi_{k_l}^*(\mathbf{r}_1) \eta_+^*(\sigma_1), \varphi_{k_l}^*(\mathbf{r}_2) \eta_+^*(\sigma_2)}{\varphi_{k_p}^*(\mathbf{r}_1) \eta_-^*(\sigma_1), \varphi_{k_p}^*(\mathbf{r}_2) \eta_-^*(\sigma_2)} \right| \Psi^{*lp;12} \right] \times \\
&\quad \times e^{i\mathbf{k}' \cdot \mathbf{r}_{12}} \frac{1}{E_0 - \hat{\mathcal{H}}_0} e^{i\mathbf{k} \cdot \mathbf{r}_{12}} \left[ \sum_{u < v}^{(+)} \left| \frac{\varphi_{k_u}(\mathbf{r}_1), \varphi_{k_u}(\mathbf{r}_2)}{\varphi_{k_v}(\mathbf{r}_1), \varphi_{k_v}(\mathbf{r}_2)} \right| \eta_+(\sigma_1) \eta_+(\sigma_2) \Psi^{uv;12} + \right. \\
&\quad \left. + \sum_{u < v}^{(-)} \left| \frac{\varphi_{k_u}(\mathbf{r}_1), \varphi_{k_u}(\mathbf{r}_2)}{\varphi_{k_v}(\mathbf{r}_1), \varphi_{k_v}(\mathbf{r}_2)} \right| \eta_-(\sigma_1) \eta_-(\sigma_2) \Psi^{uv;12} + \right. \\
&\quad \left. + \sum_u^{(+)} \sum_v^{(-)} \left| \frac{\varphi_{k_u}(\mathbf{r}_1) \eta_+(\sigma_1), \varphi_{k_u}(\mathbf{r}_2) \eta_+(\sigma_2)}{\varphi_{k_v}(\mathbf{r}_1) \eta_-(\sigma_1), \varphi_{k_v}(\mathbf{r}_2) \eta_-(\sigma_2)} \right| \Psi^{uv;12} \right] \\
&= \frac{(N'-2)!}{N'!} \frac{2m^{**}}{\hbar^2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \left\{ \left( \sum_{l < p}^{(+)} + \right. \right. \\
&\quad \left. \left. + \sum_{l < p}^{(-)} \right) \left| \frac{\varphi_{k_l}^*(\mathbf{r}_1), \varphi_{k_l}^*(\mathbf{r}_2)}{\varphi_{k_p}^*(\mathbf{r}_1), \varphi_{k_p}^*(\mathbf{r}_2)} \right| e^{i\mathbf{k}' \cdot \mathbf{r}_{12}} \frac{1}{k_l^2 + k_p^2 + \nabla_1^2 + \nabla_2^2} e^{i\mathbf{k} \cdot \mathbf{r}_{12}} \left| \frac{\varphi_{k_l}(\mathbf{r}_1), \varphi_{k_l}(\mathbf{r}_2)}{\varphi_{k_p}(\mathbf{r}_1), \varphi_{k_p}(\mathbf{r}_2)} \right| + \right. \\
&\quad \left. + \sum_l^{(+)} \sum_p^{(-)} \left[ \frac{\varphi_{k_l}^*(\mathbf{r}_1) \varphi_{k_p}^*(\mathbf{r}_2)}{\varphi_{k_l}^*(\mathbf{r}_1) \varphi_{k_p}^*(\mathbf{r}_2)} e^{i\mathbf{k}' \cdot \mathbf{r}_{12}} \frac{1}{k_l^2 + k_p^2 + \nabla_1^2 + \nabla_2^2} e^{i\mathbf{k} \cdot \mathbf{r}_{12}} \varphi_{k_l}(\mathbf{r}_1) \varphi_{k_p}(\mathbf{r}_2) + \right. \right. \\
&\quad \left. \left. + \varphi_{k_p}^*(\mathbf{r}_1) \varphi_{k_l}^*(\mathbf{r}_2) e^{i\mathbf{k}' \cdot \mathbf{r}_{12}} \frac{1}{k_l^2 + k_p^2 + \nabla_1^2 + \nabla_2^2} e^{i\mathbf{k} \cdot \mathbf{r}_{12}} \varphi_{k_p}(\mathbf{r}_1) \varphi_{k_l}(\mathbf{r}_2) \right] \right\} \\
&= \frac{1}{N'(N'-1)} \frac{2m^{**}}{\nabla^2 \hbar^2} \times \left\{ \left( \sum_{l < p}^{(+)} + \right. \right. \\
&\quad \left. \left. + \sum_{l < p}^{(-)} \right) \iint d\mathbf{r}_1 d\mathbf{r}_2 \left[ e^{-i(\mathbf{k}_l - \mathbf{k}') \cdot \mathbf{r}_1 - i(\mathbf{k}_p + \mathbf{k}') \cdot \mathbf{r}_2} \frac{1}{k_l^2 + k_p^2 + \nabla_1^2 \nabla_2^2} e^{i(\mathbf{k}_l + \mathbf{k}) \cdot \mathbf{r}_1 + i(\mathbf{k}_p - \mathbf{k}) \cdot \mathbf{r}_2} + \right. \right. \\
&\quad \left. \left. + e^{-i(\mathbf{k}_p - \mathbf{k}') \cdot \mathbf{r}_1 - i(\mathbf{k}_l + \mathbf{k}') \cdot \mathbf{r}_2} \frac{1}{k_l^2 + k_p^2 + \nabla_1^2 \nabla_2^2} e^{i(\mathbf{k}_p + \mathbf{k}) \cdot \mathbf{r}_1 + i(\mathbf{k}_l - \mathbf{k}) \cdot \mathbf{r}_2} \right] \right\}
\end{aligned}$$

$$\begin{aligned}
& e^{-i(\mathbf{k}_l - \mathbf{k}') \cdot \mathbf{r}_1 - i(\mathbf{k}_p + \mathbf{k}') \cdot \mathbf{r}_2} \frac{1}{k_l^2 + k_p^2 + V_1^2 + V_2^2} e^{i(\mathbf{k}_p + \mathbf{k}) \cdot \mathbf{r}_1 + i(\mathbf{k}_l - \mathbf{k}) \cdot \mathbf{r}_2} - \\
& - e^{-i(\mathbf{k}_p - \mathbf{k}') \cdot \mathbf{r}_1 - i(\mathbf{k}_l + \mathbf{k}') \cdot \mathbf{r}_2} \frac{1}{k_l^2 + k_p^2 + V_1^2 + V_2^2} e^{i(\mathbf{k}_l + \mathbf{k}) \cdot \mathbf{r}_1 + i(\mathbf{k}_p - \mathbf{k}) \cdot \mathbf{r}_2} \Big] + \\
& + \sum_l^{(+)} \sum_p^{(-)} \iint d\mathbf{r}_1 d\mathbf{r}_2 \left[ e^{-i(\mathbf{k}_l - \mathbf{k}') \cdot \mathbf{r}_1 - i(\mathbf{k}_p + \mathbf{k}') \cdot \mathbf{r}_2} \frac{1}{k_l^2 + k_p^2 + V_1^2 + V_2^2} \times \right. \\
& \times e^{i(\mathbf{k}_l + \mathbf{k}) \cdot \mathbf{r}_1 + i(\mathbf{k}_p - \mathbf{k}) \cdot \mathbf{r}_2} + \\
& \left. + e^{-i(\mathbf{k}_p - \mathbf{k}') \cdot \mathbf{r}_1 - i(\mathbf{k}_l + \mathbf{k}') \cdot \mathbf{r}_2} \frac{1}{k_l^2 + k_p^2 + V_1^2 + V_2^2} e^{i(\mathbf{k}_p + \mathbf{k}) \cdot \mathbf{r}_1 + i(\mathbf{k}_l - \mathbf{k}) \cdot \mathbf{r}_2} \right] \Big\} \\
& = \frac{1}{N'(N'-1)} \frac{2m^{**}}{V^2 \hbar^2} \left\{ \left( \sum_{l < p}^{(+)} + \sum_{l < p}^{(-)} \right) \left[ \frac{1}{k_l^2 + k_p^2 - (\mathbf{k}_l - \mathbf{k})^2 - (\mathbf{k}_p + \mathbf{k})^2} V^2 \delta(\mathbf{k} + \mathbf{k}') + \right. \right. \\
& + \frac{1}{k_l^2 + k_p^2 - (\mathbf{k}_l + \mathbf{k})^2 - (\mathbf{k}_p - \mathbf{k})^2} V^2 \delta(\mathbf{k} + \mathbf{k}') - \\
& - \frac{1}{k_l^2 + k_p^2 - (\mathbf{k}_l - \mathbf{k})^2 - (\mathbf{k}_p + \mathbf{k})^2} V^2 \delta(\mathbf{k} + \mathbf{k}' - \mathbf{k}_{lp}) - \\
& - \frac{1}{k_l^2 + k_p^2 - (\mathbf{k}_l + \mathbf{k})^2 - (\mathbf{k}_p - \mathbf{k})^2} V^2 \delta(\mathbf{k} + \mathbf{k}' + \mathbf{k}_{lp}) + \\
& + \sum_l^{(+)} \sum_p^{(-)} \left[ \frac{1}{k_l^2 + k_p^2 - (\mathbf{k}_l - \mathbf{k})^2 - (\mathbf{k}_p + \mathbf{k})^2} \times \right. \\
& \times V^2 \delta(\mathbf{k} + \mathbf{k}') + \frac{1}{k_l^2 + k_p^2 - (\mathbf{k}_l + \mathbf{k})^2 - (\mathbf{k}_p - \mathbf{k})^2} V^2 \delta(\mathbf{k} + \mathbf{k}') \Big] \Big\}. \quad (4.9b)
\end{aligned}$$

With respect to eq. (4.9b), the expression (4.3) becomes

$$\varepsilon_2 = \varepsilon_2^{(a)} + \varepsilon_2^{(b)}, \quad (4.10a)$$

where

$$\varepsilon_2^{(a)} = - \frac{32\pi^2}{V^2} \frac{m^{**}}{m} \sum_{l < p} \sum_{|\mathbf{k}| < k_c} \frac{1}{k_l^2} \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{k}_{lp}} \text{Ry}, \quad (4.10b)$$

$$\varepsilon_2^{(b)} = \frac{32\pi^2}{V^2} \frac{m^{**}}{m} \left( \sum_{l < p}^{(+)} + \sum_{l < p}^{(-)} \right) \sum_{\substack{|\mathbf{k}| < k_c \\ |\mathbf{k} + \mathbf{k}_{lp}| > k_c}} \frac{1}{k_l^2} \frac{1}{(\mathbf{k} + \mathbf{k}_{lp})^2} \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{k}_{lp}} \text{Ry}, \quad (4.10c)$$

$$\mathbf{k}_{lp} = \mathbf{k}_l - \mathbf{k}_p.$$



Averaging the two second order energy shifts (4.10b) and (4.10c) over all values of the wave vectors  $\mathbf{k}_i$  and  $\mathbf{k}_p$  within the Fermi sphere (I 3.12), we obtain (per one individual particle),

$$\begin{aligned} \varepsilon_2^{(a)} = & \left\{ 1.0000 - \frac{0.6079}{\alpha} - 0.5120 \cdot \alpha - 0.1013 \cdot \alpha^2 + 0.1230 \cdot \alpha^3 + \left[ -0.0853 + \right. \right. \\ & + \left. \frac{0.3843}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \right] \cdot \alpha^4 - \left[ 0.0161 + \frac{0.6321}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \right] \cdot \alpha^5 + \frac{0.3226 \cdot \alpha^6}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} + \\ & + \left. \left[ 0.2026 \cdot \alpha - 0.0034 \cdot \alpha^3 + 0.0338 \cdot \alpha^4 - \frac{0.1281 \cdot \alpha^5}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \right] \ln \alpha \right\} \text{Ry} \quad (4.11a) \end{aligned}$$

and

$$\begin{aligned} \varepsilon_2^{(b)} = & \left\{ 1.7996 - 1.5388 \cdot \alpha - 0.2749 \cdot \alpha^2 + \left[ 0.3249 - \frac{0.0253}{(2 - \alpha)^2} \right] \cdot \alpha^3 - 0.2502 \cdot \alpha^4 - \right. \\ & - \left[ 0.0479 + \frac{1.1322}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \right] \cdot \alpha^5 + \frac{0.9592 \cdot \alpha^6 + 0.1872 \cdot \alpha^7}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} - \left[ 0.4766 + \right. \\ & + 0.6079 \cdot \alpha + 0.0681 \cdot \alpha^3 + 0.1013 \cdot \alpha^4 - \frac{0.3013 \cdot \alpha^5 + 0.3843 \cdot \alpha^6}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \left. \right] \ln \alpha + \\ & + 0.0169 \ln^2 \alpha + \left[ -1.0845 - 0.1695 \cdot \alpha^3 + \frac{0.6855 \cdot \alpha^5}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \right] \ln (2 - \alpha) - \\ & \left. - 0.0169 \ln^2 (2 - \alpha) \right\} \text{Ry}. \quad (4.11b) \end{aligned}$$

Both quantities are evaluated in the Appendix.

Adding  $\varepsilon_2^{(a)}$  and  $\varepsilon_2^{(b)}$ , we have

$$\begin{aligned} \varepsilon_2 = & \left\{ -\frac{0.6079}{\alpha} + 2.7996 - 2.0508 \cdot \alpha - 0.3762 \cdot \alpha^2 + \left[ 0.4479 - \frac{0.0253}{(2 - \alpha)^2} \right] \cdot \alpha^3 + \right. \\ & + \left[ -0.3355 + \frac{0.3843}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \right] \cdot \alpha^4 - \left[ 0.0658 + \frac{1.7643}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \right] \cdot \alpha^5 + \\ & + \frac{1.2828 \cdot \alpha^6 + 0.1872 \cdot \alpha^7}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} + \left[ 0.4766 + 0.8105 \cdot \alpha + 0.0647 \cdot \alpha^3 + 0.1351 \cdot \alpha^4 - \right. \\ & - \frac{0.4294 \cdot \alpha^5 + 0.3843 \cdot \alpha^6}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \left. \right] \cdot \ln \alpha + 0.0169 \cdot \ln^2 \alpha + \left[ -1.0845 - 0.1695 \cdot \alpha^3 + \right. \\ & + \frac{0.6855 \cdot \alpha^5}{r_s^{1/2} (1 + \frac{1}{6} \alpha^3)^{1/6}} \left. \right] \cdot \ln (2 - \alpha) - 0.0169 \cdot \ln^2 (2 - \alpha) \left. \right\} \text{Ry}. \quad (4.12) \end{aligned}$$

It can be seen from eq. (4.11a) that  $\varepsilon_2^{(a)}$  has a divergence ( $\alpha \rightarrow 0$ ) of type  $\alpha^{-1}$ , whereas, according to Brueckner (1958), it is of logarithmical type one,

$$\varepsilon_2^{(a)} = -\frac{3}{2\pi^3} \int \frac{d\vec{q}}{q^3} \int_0^1 dx \int_0^1 dy \frac{x \cdot y}{x + y}.$$

This discrepancy seems to be due to Brueckner's approximate integration as opposed to the computation given in the Appendix to the present paper. As to the term  $\varepsilon_2^{(b)}$ , eq. (4.11b), it diverges as  $\ln^2 \alpha$ , whereas Brueckner found it to be regular at  $\alpha = 0$ .

The second order energy correction eq. (4.12) depends upon the spacing parameter  $r_s$  due to the presence of the quotient  $\frac{m^{**}}{m}$ , eq. (2.16).

In order to compute  $\varepsilon_2$  we utilize the values for  $\alpha$  listed in Table I. This yields the following Table III and the Fig. 1.

Table III

$r$	1	2	3	4	5	6
$\varepsilon_2^{(a)}$ Ry	-0.5699	-0.4218	-0.3429	-0.2920	-0.2583	-0.2337
$\varepsilon_2^{(b)}$ Ry	-0.0109	-0.0096	-0.0100	-0.0107	-0.0114	-0.0119
$\varepsilon_2$ Ry	-0.5808	-0.4314	-0.3529	-0.3027	-0.2697	-0.2456

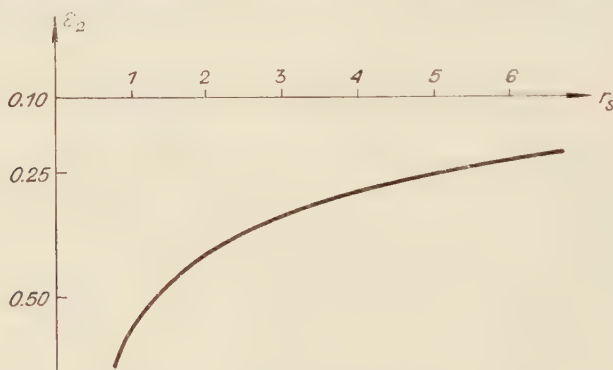


Fig. 1

It is now clear that the second order energy correction (4.12), if added to the correlation energy, lowers the latter many times. This is for the most part due to  $\varepsilon_2^{(a)}$ . It may be hoped that the successive higher order shifts would reduce the enormous contribution of  $\varepsilon_2^{(a)}$ , but it is not possible to verify this conclusion, since the Rayleigh-Schroedinger perturbation series for  $r_s > 1$  is divergent. Therefore we choose the following procedure: in part I we made use of the fact that the longitudinal vector potential is defined to a constant and we introduced its zero component  $q_0$ , which we put

$$\frac{2\pi N'e^2}{mV} q_0^2 = \frac{N'(N'-1)}{\pi V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \int_0^{k_c|\mathbf{r}-\mathbf{r}'|} d\tau \frac{\sin \tau}{\tau}, \quad (I 3.36f)$$

so as to obtain zero electrostatic energy. Since the term  $\varepsilon_2^{(a)}$  is of Coulomb integral type structure, we may now extend the definition of  $q_0$ ,

$$\frac{2\pi N'e^2}{mV} q_0^2 = \frac{N'(N'-1)}{\pi V^2} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \int_0^{k_c|\mathbf{r}-\mathbf{r}'|} d\tau \frac{\sin \tau}{\tau} - N' \varepsilon_2^{(a)}. \quad (4.13)$$

Thus, only the second correction  $\varepsilon_2^{(b)}$  remains, which we incorporate into the correlation energy. This yields

$$E_{\text{corr}}^{\dagger\ddagger} = \left\{ -0.0921 + 0.0622 \cdot \ln r_s + \frac{1}{6} 0.34373 \cdot r_s + \frac{1}{24} (-1.1449 \cdot r_s^2 + 0.3328 \cdot r_s^3 - 0.0445 \cdot r_s^4) + \frac{1}{12} 0.00114 \cdot r_s^5 \right\} \text{ Ry.} \quad (4.14)$$

The constant in the correlation energy is now by nearly 4% larger than that of Gell-Mann and Brueckner (1957).

## 5. Conclusions

In the first part of the present paper, a collective approach without subsidiary conditions is proposed. It was assumed that the collective oscillations of the charge density are excited by the colliding electrons and the electron-hole pairs appearing thereafter. Both phenomena — the electron-hole pairs and the collective oscillations related to them — were described with the help of the effective longitudinal field. The theory thus formulated allowed to calculate the magnitude of the correlation energy to the first order.

In the present paper, we effected the isolation of the plasmons and computed the second order correction to the correlation energy. Up to the first order, the constant in the correlation energy is approximately 20% larger than the same quantity obtained by Gell-Mann and Brueckner. Together with part of the second order shift, the constant becomes larger by about 4% than that calculated by these authors.

As we have already mentioned, Gell-Mann and Brueckner applied approximate integration when averaging over the Fermi distribution, considering the probability for exciting the electrons from the neighbourhood of the Fermi surface as being 1 and the probability of raising electrons from the depth of the Fermi sphere onto external orbitals as being zero. Such approximation gives rise to some error in the correlation energy constant.

The method of determining the correlation energy constant (interpolation curve for the correlation energy) used throughout the present paper involves a degree of uncertainty residing in the choice of the expansion in  $r_s$ . No such complete expansion is available, neither is one given in the Gell-Mann and Brueckner theory, as the latter retains linked cluster subseries only, whereas the processes called “non-ring”, including correlation effects due to the Pauli Principle, are neglected.

The author wishes to thank Professor Dr S. Szczeniowski for his interest throughout the present investigation.

## Appendix

We first prove the correctness of eq. (4.11a). For this purpose we write  $\varepsilon_2^{(a)}$  in the form of eq. (4.10b).

$$\varepsilon_2^{(a)} = - \frac{32\pi^2}{V^2} \frac{m^{**}}{m} \sum_{l < p} \sum_{|\mathbf{k}| > k_c} \frac{1}{k^4} \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{k}_{lp}} \text{ Ry.} \quad (4.10b)$$

Let us, for the time being, write

$$\mathbf{k}_{lp} = \mathbf{a} = a \mathbf{z}^0,$$

where  $\mathbf{z}^0$  is the unit vector in the direction of the  $z$ -axis. We have

$$\begin{aligned} A &= \sum_{|\mathbf{k}| > k_c} \frac{1}{k^4} \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{a}} = \frac{V}{(2\pi)^3} \int_{|\mathbf{k}| > k_c} \frac{d\mathbf{k}}{k^5} \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{a}} = \frac{V}{4\pi^2} \int_{k_c}^{+\infty} \frac{dk}{k^2} \int_{-1}^{+1} \frac{d\tau}{k^2 + ka\tau} = \\ &= \frac{V}{4\pi^2 a} \int_{k_c}^{+\infty} \frac{dk}{k^3} [\ln(k+a) - \ln|k-a|] = \frac{V}{8\pi^2 a} \left[ \frac{2}{k_c a} + \left( \frac{1}{k_c^2} - \frac{1}{a^2} \right) \ln \frac{k_c + a}{k_c - a} \right]. \end{aligned} \quad (\text{A.1})$$

We now average the expression (A.1) over the Fermi distribution (I 3.12) for  $\vartheta = \frac{1}{2}$ , obtaining

$$\langle A \rangle = \frac{V}{8\pi^2} \frac{1}{\left( \frac{4\pi k_F^3}{3} \right)^2} \int d\mathbf{k}_l \int d\mathbf{k}_p \left[ \frac{2}{k_c k_{lp}^2} + \left( \frac{1}{k_c^2 k_{lp}} - \frac{1}{k_{lp}^3} \right) \ln \frac{k_c + k_{lp}}{|k_c - k_{lp}|} \right]. \quad (\text{A.2})$$

On substitution of

$$\begin{aligned} \mathbf{k}_l - \mathbf{k}_p &= \vec{\varrho}, & \mathbf{k}_l &= \mathbf{R} + \frac{1}{2} \vec{\varrho}, & |\mathbf{k}_l| &= |\mathbf{R} + \frac{1}{2} \vec{\varrho}| \leq k_F, \\ \mathbf{k}_l + \mathbf{k}_p &= 2\mathbf{R}, & \mathbf{k}_p &= \mathbf{R} - \frac{1}{2} \vec{\varrho}, & |\mathbf{k}_p| &= |\mathbf{R} - \frac{1}{2} \vec{\varrho}| \leq k_F, \end{aligned} \quad d\mathbf{k}_l d\mathbf{k}_p = d\mathbf{R} d\vec{\varrho}, \quad (\text{A.3})$$

eq. (A.2) transforms to

$$\begin{aligned} \langle A \rangle &= \frac{V}{8\pi^2} \frac{1}{\left( \frac{4\pi k_F^3}{3} \right)^2} \int d\vec{\varrho} \left[ \frac{2}{k_c \varrho^2} + \frac{1}{\varrho} \left( \frac{1}{k_c^2} - \frac{1}{\varrho^2} \right) \times \right. \\ &\quad \left. \times \ln \frac{k_c + \varrho}{|k_c - \varrho|} \right] \int_{\substack{|\mathbf{R} + \frac{1}{2}\vec{\varrho}| \leq k_F \\ |\mathbf{R} - \frac{1}{2}\vec{\varrho}| \leq k_F}} d\mathbf{R}. \end{aligned} \quad (\text{A.4})$$

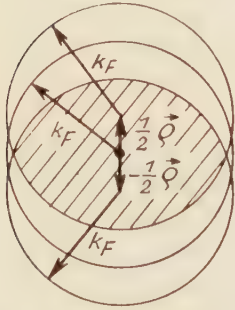


Fig. 2 Allowed region (shaded) for  $\mathbf{R}$  integration

We evaluate the second integral of eq. (A.4) in cylindrical coordinates,

$$\begin{aligned} \int_{\substack{|\mathbf{R} + \frac{1}{2}\vec{\varrho}| \leq k_F \\ |\mathbf{R} - \frac{1}{2}\vec{\varrho}| \leq k_F}} d\mathbf{R} &= 2 \cdot 2\pi \int_0^{\sqrt{k_F^2 - \frac{1}{4}\varrho^2}} dr \cdot r \int_{\frac{1}{2}\varrho}^{\sqrt{k_F^2 - r^2}} dz = 4\pi \int_0^{\sqrt{k_F^2 - \frac{1}{4}\varrho^2}} dr \cdot r \left( \sqrt{k_F^2 - r^2} - \frac{1}{2} \varrho \right) \\ &= \pi \left( \frac{4}{3} k_F^3 - k_F^2 \varrho + \frac{1}{12} \varrho^3 \right). \end{aligned} \quad (\text{A.5})$$



Reverting to eq. (A.4), we have

$$\begin{aligned}
\langle A \rangle &= \frac{9V}{32\pi^2 k_F^6} \int_{\varrho \leq 2k_F} d\varrho \cdot \varrho^2 \left[ \frac{2}{k_c \varrho^2} + \frac{1}{\varrho} \left( \frac{1}{k_c^2} - \frac{1}{\varrho^2} \right) \ln \frac{\varrho + k_c}{|\varrho - k_c|} \right] \left( \frac{4}{3} k_F^3 - k_F^2 \varrho + \right. \\
&+ \left. \frac{1}{12} \varrho^3 \right) = \frac{9V}{32\pi^2 k_F^6} \left\{ \int_0^{2k_F} d\varrho \left( \frac{8}{3} \frac{k_F^3}{k_c} - 2 \frac{k_F^2}{k_c} \varrho + \frac{1}{6k_c} \varrho^3 \right) + \int_{\varrho \leq 2k_F} d\varrho \left[ -\frac{4}{3} k_F^3 \frac{1}{\varrho} + \right. \right. \\
&+ \left. \left. k_F^2 + \frac{4}{3} \frac{k_F^2}{k_c^2} \varrho - \left( \frac{k_F^2}{k_c^2} + \frac{1}{12} \right) \varrho^2 + \frac{1}{12 k_c^2} \varrho^4 \right] \cdot \ln \frac{\varrho + k_c}{|\varrho - k_c|} \right\} \\
&= \frac{9V}{32\pi^2 k_F^6} \left[ \frac{52}{15} \frac{1}{\alpha} - \frac{2}{3} \pi^2 + \frac{58}{45} \alpha + \frac{1}{27} \alpha^3 + \frac{1}{300} \alpha^5 + \left( \frac{4}{3} \alpha - \frac{\alpha^3}{45} \right) \ln 2 + \right. \\
&+ \left( -\frac{4}{3} \alpha + \frac{1}{45} \alpha^3 \right) \cdot \ln \alpha + \left( \frac{8}{15\alpha^2} + \frac{10}{9} + \frac{2}{3} \alpha - \frac{1}{90} \alpha^3 \right) \cdot \ln \left( 1 + \frac{\alpha}{2} \right) + \\
&+ \left. \left( -\frac{8}{15\alpha^2} - \frac{10}{9} + \frac{2}{3} \alpha - \frac{1}{90} \alpha^3 \right) \cdot \ln \left( 1 - \frac{\alpha}{2} \right) \right]. \quad (\text{A.6})
\end{aligned}$$

All integrations in eq. (A.6) are elementary except one integral, namely

$$\begin{aligned}
\int_{\varrho \leq 2k_F} \frac{d\varrho}{\varrho} \ln \frac{\varrho + k_c}{|\varrho - k_c|} &= \int_0^{k_c} \frac{d\varrho}{\varrho} \ln \frac{1 + \varrho/k_c}{1 - \varrho/k_c} + \int_{k_c}^{2k_F} \frac{d\varrho}{\varrho} \ln \frac{1 + k_c/\varrho}{1 - k_c/\varrho} = \int_0^1 \frac{d\tau}{\tau} \ln \frac{1 + \tau}{1 - \tau} + \\
&+ \int_{\alpha/2}^1 \frac{d\tau}{\tau} \ln \frac{1 + \tau}{1 - \tau} = 2 \int_0^1 \frac{d\tau}{\tau} \ln \frac{1 + \tau}{1 - \tau} - \int_0^{\alpha/2} \frac{d\tau}{\tau} \ln \frac{1 + \tau}{1 - \tau},
\end{aligned}$$

where  $\alpha = \frac{k_c}{k_F} < 1$ .

The last two integrals are readily computed by expanding  $\ln \frac{1 + \tau}{1 - \tau}$ . This yields

$$\begin{aligned}
\int_{\varrho \leq 2k_F} \frac{d\varrho}{\varrho} \ln \frac{\varrho + k_c}{|\varrho - k_c|} &= 4 \sum_{s=0}^{+\infty} \frac{1}{2s+1} \int_0^1 d\tau \cdot \tau^{2s} - 2 \sum_{s=0}^{+\infty} \frac{1}{2s+1} \int_0^{\alpha/2} d\tau \cdot \tau^{2s} \\
&= 4 \sum_{s=0}^{+\infty} \frac{1}{(2s+1)^2} - 2 \sum_{s=0}^{+\infty} \frac{1}{(2s+1)^2} \left( \frac{\alpha}{2} \right)^{2s+1} = \frac{\pi^2}{2} - 2 \sum_{s=0}^{+\infty} \frac{1}{(2s+1)^2} \left( \frac{\alpha}{2} \right)^{2s+1},
\end{aligned}$$

as the sum  $4 \sum_{s=1}^{+\infty} \frac{1}{(2s+1)^2}$  is the derivative of the logarithmical derivative  $\Psi(1/2)$  (Jahnke and Emde 1959).

In order to complete our computation, we still have to expand  $\ln \left( 1 + \frac{\alpha}{2} \right)$  and

$\ln \left(1 - \frac{\alpha}{2}\right)$  in eq. (A.6) (we retain only the terms up to  $\alpha^5$ ) and to insert the expression obtained into eq. (4.10b). The result is eq. (4.11a).

We proceed now to the evaluation of the energy correction (4.11b). We have

$$\varepsilon_2^{(b)} = \frac{32\pi^2 m^{**}}{f^2 m} \left( \sum_{l < p}^{(+)} + \sum_{l < p}^{(-)} \right) \sum_{\substack{|\mathbf{k}| > k_c \\ |\mathbf{k} + \mathbf{k}_{lp}| > k_c}} \frac{1}{k^2} \frac{1}{(\mathbf{k} + \mathbf{k}_{lp})^2} \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{k}_{lp}} \text{Ry.} \quad (4.10c)$$

Let us denote

$$B(\mathbf{k}, \mathbf{a}) = \frac{1}{(\mathbf{k} + \mathbf{a})^2} \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{a}} = \frac{1}{a^2 - k^2} \left( \frac{1}{k^2 - \mathbf{k} \cdot \mathbf{a}} - \frac{2}{k^2 + a^2 + 2\mathbf{k} \cdot \mathbf{a}} \right) \quad (A.7a)$$

and substitute

$$\mathbf{a} = \mathbf{k}_l - \mathbf{k}_p, \quad 2\mathbf{b} = \mathbf{k}_l + \mathbf{k}_p, \quad d\mathbf{k}_l \cdot d\mathbf{k}_p = d\mathbf{a} \cdot d\mathbf{b}.$$

The mean over the Fermi distribution is now

$$\begin{aligned} \langle B(\mathbf{k}, \mathbf{a}) \rangle &= B(\mathbf{k}) = \frac{9}{16\pi^2 k_F^6} \int d\mathbf{k}_l \int d\mathbf{k}_p \frac{1}{k_{lp}^2 - k^2} \left( \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{k}_{lp}} - \right. \\ &\quad \left. - \frac{2}{k^2 + k_{lp}^2 + 2\mathbf{k} \cdot \mathbf{k}_{lp}} \right) = \frac{9}{16\pi^2 k_F^6} \int_{\substack{|\mathbf{a} + \mathbf{k}| \geq k_c \\ |\mathbf{a}| \leq 2k_F}} d\mathbf{a} \frac{1}{a^2 - k^2} \left( \frac{1}{k^2 - \mathbf{k} \cdot \mathbf{a}} - \right. \\ &\quad \left. - \frac{2}{k^2 + a^2 + 2\mathbf{k} \cdot \mathbf{a}} \right) \int_{\substack{|\mathbf{b} + \frac{1}{2}\mathbf{a}| \leq k_F \\ |\mathbf{b} - \frac{1}{2}\mathbf{a}| \leq k_F}} d\mathbf{b} = \frac{9}{16\pi k_F^6} \int_{\substack{|\mathbf{a} + \mathbf{k}| \geq k_c \\ |\mathbf{a}| \leq 2k_F}} d\mathbf{a} \frac{1}{a^2 - k^2} \left( \frac{1}{k^2 - \mathbf{k} \cdot \mathbf{a}} - \right. \\ &\quad \left. - \frac{2}{k^2 + a^2 + 2\mathbf{k} \cdot \mathbf{a}} \right) \cdot \left( \frac{4}{3} k_F^3 - ak_F^2 + \frac{1}{12} a^3 \right). \end{aligned} \quad (A.7b)$$

We assume the  $\mathbf{k}$ -vector to be directed along the  $z$ -axis. There are three stages of integration illustrated below

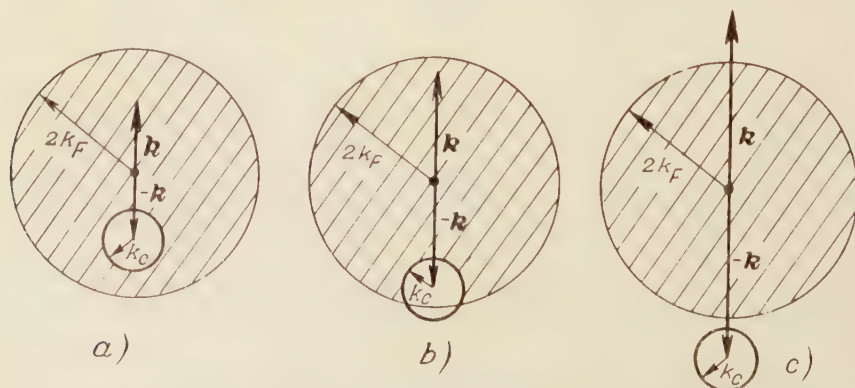


Fig. 3 Allowed regions (shaded) for  $\mathbf{a}$  integration for: a)  $k_c \leq k \leq 2k_F - k_c$ , b)  $2k_F - k_c \leq k \leq 2k_F + k_c$ , c)  $2k_F + k_c \leq k \leq +\infty$ .

Since the contribution from small  $\mathbf{k}$  are the most essential for the integral (4.10c), we restrict our computation to the case  $a$ ). The integration now consists in taking the integral over the sphere of radius  $2k_F$  minus the integration within the  $k_c$ -radius sphere. We have then

$$B(\mathbf{k}) = \frac{9}{16\pi k_F^6} [B^{(1)}(\mathbf{k}) - B^{(2)}(\mathbf{k})], \quad (\text{A.7c})$$

with

$$B^{(1)}(\mathbf{k}) = \int_{|\mathbf{a}| \leq 2k_F} d\mathbf{a} \frac{1}{a^2 - k^2} \left( \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{a}} - \frac{2}{k^2 + a^2 + 2\mathbf{k} \cdot \mathbf{a}} \right) \cdot \left( \frac{4}{3} k_F^3 - ak_F^2 + \frac{1}{12} a^3 \right), \quad (\text{A.7d})$$

$$B^{(2)}(\mathbf{k}) = \int_{|\mathbf{a} + \mathbf{k}| \leq k_c} d\mathbf{a} \frac{1}{(\mathbf{k} + \mathbf{a})^2} \frac{1}{\mathbf{k} \cdot (\mathbf{k} + \mathbf{a})} \left( \frac{4}{3} k_F^3 - ak_F^2 + \frac{1}{12} a^3 \right). \quad (\text{A.7e})$$

$B^{(1)}(\mathbf{k})$  is now

$$\begin{aligned} B^{(1)}(\mathbf{k}) &= 2\pi \int_{a \leq 2k_F} \frac{da \cdot a^2}{a^2 - k^2} \left( \frac{4}{3} k_F^3 - a \cdot k_F^2 + \frac{1}{12} a^3 \right) \int_{-1}^{+1} d\tau \left( \frac{1}{k^2 + ka\tau} - \right. \\ &\quad \left. - \frac{2}{k^2 + a^2 + 2ka\tau} \right) = \frac{2\pi}{k} \int_{a \leq 2k_F} \frac{da \cdot a}{a^2 - k^2} \left( \frac{4}{3} k_F^3 - ak_F^2 + \frac{1}{12} a^3 \right) [\ln(k^2 + ka\tau) - \\ &\quad - \ln(k^2 + a^2 + 2ka\tau)]_{-1}^{+1} = \frac{2\pi}{k} \int_{a \leq 2k_F} \frac{da \cdot a}{a^2 - k^2} \left( \frac{4}{3} k_F^3 - ak_F^2 + \frac{1}{12} a^3 \right) \cdot \left( \ln \frac{a+k}{|a-k|} - \right. \\ &\quad \left. - 2 \ln \frac{a+k}{|a-k|} \right) = - \frac{2\pi}{k} \int_{a \leq 2k_F} \frac{da \cdot a}{a^2 - k^2} \left( \frac{4}{3} k_F^3 - ak_F^2 + \frac{1}{12} a^3 \right) \ln \frac{a+k}{|a-k|} \\ &= - \frac{2\pi}{k} \left[ - \int_0^k \frac{da \cdot a}{k^2 - a^2} \left( \frac{4}{3} k_F^3 - ak_F^2 + \frac{1}{12} a^3 \right) \ln \frac{k+a}{k-a} + \int_k^{2k_F} \frac{da \cdot a}{a^2 - k^2} \left( \frac{4}{3} k_F^3 - \right. \right. \\ &\quad \left. \left. - ak_F^2 + \frac{1}{12} a^3 \right) \ln \frac{a+k}{a-k} \right] = \frac{2\pi}{k} \left[ \int_0^1 \frac{d\tau \cdot \tau}{1 - \tau^2} \left( \frac{4}{3} k_F^3 - \tau k k_F^2 + \frac{1}{12} \tau^3 k^3 \right) \ln \frac{1+\tau}{1-\tau} - \right. \\ &\quad \left. - \int_{x/2}^1 \frac{d\tau}{\tau(1-\tau^2)} \left( \frac{4}{3} k_F^3 - \frac{k k_F^2}{\tau} + \frac{k^3}{12\tau^3} \right) \ln \frac{1+\tau}{1-\tau} \right] = \frac{2\pi}{x} k_F^2 \left[ - \frac{\pi^2}{3} + \frac{2}{9} \ln 2 + \right. \\ &\quad \left. + (3 + 2 \ln 2)x - 2x \ln x - \frac{2}{9} \ln x - \frac{10}{27} x^3 + \right. \\ &\quad \left. + 8 \sum_{n=0}^{+\infty} \frac{1}{(2n+2)(2n+4)(2n+5)} \left( \frac{x}{2} \right)^{2n+5} \sum_{i=0}^{n+2} \frac{1}{(2i+1)} \right], \quad x = \frac{k}{k_F}. \quad (\text{A.7f}) \end{aligned}$$

In the term (A.7e), we substitute  $\mathbf{k} + \mathbf{a} = \mathbf{b}$  obtaining

$$B^{(2)}(\mathbf{k}) = \int_{|\mathbf{b}| < k_c} d\mathbf{b} \frac{1}{b^2} \frac{1}{\mathbf{k} \cdot \mathbf{b}} \left( \frac{4}{3} k_F^3 - |\mathbf{k} - \mathbf{b}| k_F^2 + \frac{1}{12} |\mathbf{k} - \mathbf{b}|^3 \right) =$$

$$= \frac{2\pi}{k} \int_{b \leq k_c} \frac{db}{b} \int_{-1}^{+1} \frac{d\tau}{\tau} \left[ \frac{4}{3} k_F^3 - (k^2 + b^2 - 2kb\tau)^{1/2} k_F^2 + \frac{1}{12} (k^2 + b^2 - 2kb\tau)^{3/2} \right].$$

We put

$$k^2 + b^2 - 2kb\tau = u^2, \quad k - b \leq u \leq k + b, \quad d\tau = -\frac{u}{kb} du$$

and get

$$B^{(2)}(\mathbf{k}) = \frac{2\pi}{k} \int_0^{k_c} \frac{db}{b} \left[ 2k_F^2 \int_{k+b}^{k-b} \frac{u^2 du}{k^2 + b^2 - u^2} - \frac{1}{6} \int_{k+b}^{k-b} \frac{u^4 du}{k^2 + b^2 - u^2} \right] = \frac{2\pi}{k} \int_0^{k_c} \frac{db}{b} \left\{ 2k_F^2 \times \right.$$

$$\times \int_{k+b}^{k-b} du \left( -1 + \frac{k^2 + b^2}{k^2 + b^2 - u^2} \right) - \frac{1}{6} \int_{k+b}^{k-b} du \left[ - (k^2 + b^2) - u^2 + \frac{(k^2 + b^2)^2}{k^2 + b^2 - u^2} \right] \Big\}$$

$$= \frac{2\pi}{k} \int_0^{k_c} \frac{db}{b} \left\{ -2k_F^2 [k - b - (k + b)] + k_F^2 \sqrt{k_F^2 + b^2} \int_{k+b}^{k-b} du \left( \frac{1}{\sqrt{k^2 + b^2 + u}} + \right. \right.$$

$$\left. + \frac{1}{\sqrt{k^2 + b^2 - u}} \right) + \frac{1}{6} (k^2 + b^2) [k - b - (k + b)] + \frac{1}{18} [(k - b)^3 - (k + b)^3] -$$

$$- \frac{1}{12} (k^2 + b^2)^{3/2} \int_{k+b}^{k-b} du \left( \frac{1}{\sqrt{k^2 + b^2 + u}} + \frac{1}{\sqrt{k^2 + b^2 - u}} \right) \Big\} = \frac{2\pi}{k} \left\{ 4k_F^2 k_c + \right.$$

$$+ k_F^2 \int_0^{k_c} \frac{db}{b} \sqrt{k^2 + b^2} [\ln(\sqrt{k^2 + b^2} + u)]_{k+b}^{k-b} - \ln(u - \sqrt{k^2 + b^2}) \Big|_{k+b}^{\sqrt{k^2 + b^2}} -$$

$$- \ln(\sqrt{k^2 + b^2} - u) \Big|_{\sqrt{k^2 + b^2}}^{k-b} \Big] - \frac{1}{3} k^2 k_c - \frac{1}{9} k_c^3 - \frac{1}{3} k^2 k_c - \frac{1}{27} k_b^3 -$$

$$- \frac{1}{12} \int_0^{k_c} \frac{db}{b} (k^2 + b^2)^{3/2} [\ln(\sqrt{k^2 + b^2} + u)]_{k+b}^{k-b} - \ln(u - \sqrt{k^2 + b^2}) \Big|_{k+b}^{\sqrt{k^2 + b^2}} -$$

$$- \ln(\sqrt{k^2 + b^2} - u) \Big|_{\sqrt{k^2 + b^2}}^{k-b} \Big\} = \frac{2\pi}{k} \left[ 4k_F^2 k_c - \frac{2}{3} k^2 k_c - \frac{4}{27} k_c^3 + \right.$$



$$\begin{aligned}
& + k_F^2 \int_0^{k_c} \frac{db}{b} (k^2 + b^2)^{1/2} \left( \ln \frac{\sqrt{k^2 + b^2} + k - b}{\sqrt{k^2 + b^2} + k + b} + \ln \frac{-\sqrt{k^2 + b^2} + k + b}{\sqrt{k^2 + b^2} - k + b} \right) - \\
& - \frac{1}{12} \int_0^{k_c} \frac{db}{b} (k^2 + b^2)^{1/2} \left( \ln \frac{\sqrt{k^2 + b^2} + k - b}{\sqrt{k^2 + b^2} + k + b} + \ln \frac{-\sqrt{k^2 + b^2} + k + b}{\sqrt{k^2 + b^2} - k + b} \right) \Big].
\end{aligned} \tag{A.7g}$$

Since  $b \leq k_c \leq k$ , we may expand the subintegral expressions in eq. (A.7g) in power series in  $b/k$ . Thus, we have

$$\ln(1 - x + \sqrt{1 + x^2}) = \ln 2 - \frac{1}{2}x + \frac{1}{8}x^2 + \frac{1}{12}x^3 - \frac{3}{64}x^4 - \frac{3}{80}x^5 + O(x^6),$$

$$\ln(1 + x + \sqrt{1 + x^2}) = \ln 2 + \frac{1}{2}x + \frac{1}{8}x^2 - \frac{1}{12}x^3 - \frac{3}{64}x^4 + \frac{3}{80}x^5 + O(x^6),$$

$$\ln(1 + x - \sqrt{1 + x^2}) = \ln x - \frac{1}{2}x - \frac{1}{8}x^2 + \frac{1}{12}x^3 + \frac{3}{64}x^4 - \frac{3}{80}x^5 + O(x^6),$$

$$\ln(-1 + x + \sqrt{1 + x^2}) = \ln x + \frac{1}{2}x - \frac{1}{8}x^2 - \frac{1}{12}x^3 + \frac{3}{64}x^4 + \frac{3}{80}x^5 + O(x^6),$$

and

$$\begin{aligned}
B^{(2)}(\mathbf{k}) = & \frac{2\pi}{x} k_F^2 \left[ \frac{4}{75} \frac{\alpha^5}{x^4} + \left( -\frac{2}{9} \alpha^3 + \frac{1}{150} \alpha^5 \right) \frac{1}{x^2} + 2\alpha - \right. \\
& \left. - \frac{2}{27} \alpha^3 - \frac{29}{48} \alpha \cdot x^2 \right], \quad x = \frac{k}{k_F}.
\end{aligned} \tag{A.7h}$$

With respect to eqs. (A.7f) and (A.7h), we obtain

$$\begin{aligned}
\left\langle \sum_{\substack{|\mathbf{k}| > k_c \\ |\mathbf{k} + \mathbf{a}| > k_c}} \frac{1}{k^2} \frac{1}{(\mathbf{k} + \mathbf{a})^2} \frac{1}{k^2 + \mathbf{k} \cdot \mathbf{a}} \right\rangle &= \frac{V}{8\pi^3} \frac{9}{16\pi k_F^6} \int_{k_c}^{2k_F - k_c} \frac{d\mathbf{k}}{k^2} [B^{(1)}(\mathbf{k}) - B^{(2)}(\mathbf{k})] \\
&= \frac{9V}{16\pi^2 k_F^3} \int_{\alpha}^{2-\alpha} \frac{dx}{x} \left[ \left( -\frac{\pi^2}{3} + \frac{2}{9} \ln 2 \right) + (3 + 2 \ln 2) x - 2x \ln x - \frac{2}{9} \ln x - \frac{10}{27} x^3 + \right. \\
&+ 8 \sum_{n=0}^{+\infty} \frac{1}{(2n+2)(2n+4)(2n+5)} \left( \frac{x}{2} \right)^{2n+5} \sum_{l=0}^{n+2} \frac{1}{2l+1} - \frac{4}{75} \frac{\alpha^5}{x^4} + \left( \frac{2}{9} \alpha^3 - \right. \\
&- \frac{1}{150} \alpha^5 \Big) \frac{1}{x^2} - 2\alpha + \frac{2}{27} \alpha^3 + \frac{29}{48} \alpha \cdot x^2 \Big] = \frac{9V}{16\pi^2 k_F^3} \left\{ \left( \frac{\pi^2}{3} - \frac{2}{9} \ln 2 + 4\alpha - \right. \right. \\
&- \frac{2}{27} \alpha^3 \Big) \ln \alpha + \left( -\frac{\pi^2}{3} + \frac{2}{9} \ln 2 - 4 + \frac{2}{27} \alpha^3 \right) \ln(2 - \alpha) + \frac{1}{9} \ln^2 \alpha - \\
&- \frac{1}{9} \ln^2(2 - \alpha) + \left( 9 + 4 \ln 2 + \frac{1}{81} \right) + \left( -10 - 4 \ln 2 + \frac{43}{27} + \frac{29}{24} - \frac{1}{75} \right) \alpha -
\end{aligned}$$

$$\begin{aligned}
& - \left( \frac{29}{24} + \frac{20}{27} \right) \alpha^2 + \left[ \frac{20}{81} - \frac{1}{300} - \frac{1}{9} \frac{1}{(2-\alpha)^2} \right] \cdot \alpha^3 + \frac{1}{300} \left[ 1 + \right. \\
& \left. + \frac{4}{(2-\alpha)^2} \right] \frac{\alpha^5}{(2-\alpha)^2} + \frac{23}{375} \left( 1 - \frac{1}{2} \alpha \right)^5 + \frac{176}{15435} \left( 1 - \frac{1}{2} \alpha \right)^7 + \dots \}. \quad (\text{A.7i})
\end{aligned}$$

Inserting eq. (A.7i) into eq. (4.10c) and multiplying by  $\frac{m^{**}}{m}$  we obtain, per one particle, eq. (4.11b).

It may be readily verified that a contribution from the case c) of Fig. 3 is strongly convergent and yields a small correction only.

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## THE DISTRIBUTION OF ELECTRONS IN THE PROCESS OF IMPACT IONIZATION

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The probability function of occupying the states with definite energy in the conduction band after an ionization is calculated. The valence band is assumed of finite width. Several cases of the primary energy and of the effective mass of the valence band are examined.

The electron impact ionization plays an important role in such processes occurring in insulators and semiconductors as: (1) the electric breakdown in insulators (see Franz 1952), (2) the interaction between radiation and insulators or semiconductors (see Antončík 1957), (3) the processes occurring in semiconductors under the influence of electron bombardment (see Zaręba 1959).

The electron impact ionization is a process in which a sufficiently energetic electron from the conduction band, or alternatively an electron coming from the outside of the crystal, suffers a "collision" with an electron from the valence band, so that the latter goes over to the conduction band while the primary electron remains also in the conduction band.

The theoretical treatment of the problem of the electron impact ionization was given in Tewordt's paper (1954) and later it was summarized and generalized by Franz (1956).

We shall follow here the definitions and the notation used in Franz's paper.

Franz has given the expressions for the probabilities of the electron transitions in the process of electron impact ionization. Their derivation was based on some simplifying assumptions. One of the fundamental assumption is that the electron impact ionization is considered only in that region of the wave vector space which is close to the ionization threshold.

Franz has also given an expression for the probability of occupying the states with definite energy in the conduction band after the process of ionization. This expression was given only for the case when the valence band is treated as a discrete level with a width equal to zero. It follows from this expression that the most prob-

able distribution of the surplus energy is the equal distribution between the two "colliding" electrons.

In this paper the probability of occupying the states with definite energy in the conduction band is calculated for the case of a non-zero width of the valence band.

We shall perform our calculations for the case when the ionization is caused by the electrons in the conduction band with a small energy  $E(\mathbf{k}_1)$ , namely  $J \leq E(\mathbf{k}_1) \leq \leq 2J$ , where  $\mathbf{k}_1$  is the wave vector of the primary electron. The zero of the  $E(\mathbf{k}_1)$  is taken at the bottom of the conduction band. Franz's assumption is followed that the electrons in the conduction band behave as free.  $J$  is the energy gap between the valence and the conduction bands. For the energy  $E(\mathbf{k}_1)$  within the specified limits the ionization takes only place in the region of energy close to the threshold of ionization and that takes place near the top of the valence band. In this case the assumption of a parabolic form of the valence band energy is a reasonable assumption. Furthermore in this case all the approximations made by Franz are well satisfied.

Therefore, the following expression for the energy of the valence band is assumed

$$E(\mathbf{k}_2) = -J - \frac{\hbar^2}{2m^*} \mathbf{k}_2^2, \quad (1)$$

where  $\mathbf{k}_2$  is the wave vector and  $m^*$  is the effective mass of an electron in the valence band.

The following situation is considered: an electron from the conduction band in the state determined by the wave vector  $\mathbf{k}_1$  interacts with an electron from the valence band in the state  $\mathbf{k}_2$ . After the "collision" there are two electrons in the conduction band in the states determined by  $\mathbf{k}'_1$  and  $\mathbf{k}'_2$ . In the process the laws of conservation of energy and momentum (in our case the latter is equivalent to a relation between the wave vectors) must be satisfied:

$$\mathbf{k}'_1 + \mathbf{k}'_2 = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_n = 2\mathbf{k}_0, \quad (2a)$$

$$E(\mathbf{k}'_1) + E(\mathbf{k}'_2) = E(\mathbf{k}_1) + E(\mathbf{k}_2). \quad (2b)$$

Here  $\mathbf{k}_n$  are the vectors of the reciprocal lattice. These two laws are fulfilled simultaneously if

$$K^2 = \frac{1}{2} \left[ \mathbf{k}_1^2 + \frac{2m}{\hbar^2} E(\mathbf{k}_2) \right] - \mathbf{k}_0^2 \geq 0, \quad (3)$$

where  $\mathbf{k}_0$  is a function of  $(\mathbf{k}_2 + \mathbf{k}_n)$ . From the condition  $K^2 \geq 0$ , we can determine in the valence band the region of the vectors  $(\mathbf{k}_2 + \mathbf{k}_n)$  (or alternatively  $\mathbf{k}_0$ , which we shall use later) from which, for a fixed  $\mathbf{k}_1$ , ionization is possible.

The probability of occupying the state with energy  $E(\mathbf{k}'_1)$  when the primary electron has the wave vector  $\mathbf{k}_1$  is given by the expression

$$P(\mathbf{k}_1, E(\mathbf{k}'_1)) = \frac{mV}{\hbar^2 \pi^3} \int d_3 \mathbf{k}_0 \int_0^{2\pi} d\varphi \frac{1}{k_0 K} P(\mathbf{k}_1, \mathbf{k}_0, \Omega), \quad (4)$$

where  $P(\mathbf{k}_1, \mathbf{k}_0, \Omega) = \sum_n P_n(\mathbf{k}_1, \mathbf{k}_2, \Omega)$ ,  $(\mathbf{k}_2 + \mathbf{k}_n)$  has been replaced by  $(2\mathbf{k}_0 - \mathbf{k}_1)$  and

$$P_n(\mathbf{k}_1, \mathbf{k}_2, \Omega) = \frac{2me^4}{V\hbar^3} |a(\mathbf{k}_n + \mathbf{k}_2)|^2 K \left\{ \frac{1}{(\mathbf{k}_1 - \mathbf{k}_0 - \mathbf{K})^4} + \frac{1}{(\mathbf{k}_1 - \mathbf{k}_0 + \mathbf{K})^4} - \frac{1}{(\mathbf{k}_1 - \mathbf{k}_0 - \mathbf{K})^2 (\mathbf{k}_1 - \mathbf{k}_0 + \mathbf{K})^2} \right\}. \quad (5)$$

$a(\mathbf{k}_2 + \mathbf{k}_n)$  is the Fourier component of the wave function of the valence electron.

With the approximations employed by Franz, the final expression, which will be used for the calculation of the probability function, has the form

$$P(\mathbf{k}_1, E(\mathbf{k}'_1)) = C \int \frac{d_3 \mathbf{k}_0}{k_0}, \quad (6)$$

where

$$C = \frac{4m^2 e^4 (1 + 2\mu)^4}{\pi^2 \hbar^5 (1 + \mu)^4} \cdot \frac{\left| a \left( -\frac{1}{1 + 2\mu} \mathbf{k}_1 \right) \right|^2}{k_1^4}, \quad (7)$$

and  $\mu = m/m^*$ .

In order to calculate the above integrals, we must know the region of integration in the  $\mathbf{k}_0$  space. The region of  $\mathbf{k}_0$  vectors allowed by the conservation laws is obtained from the condition  $K^2 \geq 0$ .

The primary electron with the fixed wave vector  $\mathbf{k}_1$  transfers its energy to an arbitrary electron with the wave vector  $\mathbf{k}_0$  ( $\mathbf{k}_0$  substitutes  $\mathbf{k}_2 + \mathbf{k}_n$ ) from the allowed region. However, it is easy to verify that an ionized electron with a definite energy  $E(\mathbf{k}'_1)$  cannot be ejected from every state in the allowed region of  $\mathbf{k}_0$  but only from certain states. In other words, the ionized electron can attain the energy  $E(\mathbf{k}'_1)$  by a "collision" of the electron in the state  $\mathbf{k}_1$  with any electron from a fraction of the allowed region of  $\mathbf{k}_0$  only. Thus we shall have different regions of integration for different  $E(\mathbf{k}'_1)$ .

Turning our attention to the function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$ , we must discuss its dependence on one variable  $E(\mathbf{k}'_1)$  and two parameters. The parameters are: (1) The momentum or the wave vector  $\mathbf{k}_1$  of the primary electron. Due to the spherical symmetry of the surfaces of constant energy for both the conduction and valence bands the dependence of  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  only on the magnitude of  $\mathbf{k}_1$  or on the energy  $E(\mathbf{k}_1)$  can be considered; for every direction in  $\mathbf{k}$ -space the situation is the same. (2) The parameter  $\mu$  or  $m^*$  — the effective mass near the top of the valence band.

We can go over now to the discussion of the region of integration. Firstly from the condition  $K^2 \geq 0$  we shall find the whole region of the allowed  $\mathbf{k}_0$  and in fact the region of  $2\mathbf{k}_0$ , because this latter vector appears in the relation (2a).

The solution of the equation  $K^2 = 0$  gives the boundary surface of this region. Solving this equation, we obtain

$$\left( 2\mathbf{k}_0 - \frac{2\mu}{1 + 2\mu} \mathbf{k}_1 \right)^2 = \frac{2(1 + \mu)}{(1 + 2\mu)^2} (k_1^2 - \bar{k}_1^2). \quad (8)$$



$\frac{\hbar^2}{2m} \bar{k}_1^2$  is the smallest energy of the conduction electron for which the impact ionization begins. It depends on the size of the energy gap and on the effective mass:

$$\frac{\hbar^2}{2m} \bar{k}_1^2 = \frac{1 + 2\mu}{1 + \mu} J. \quad (9)$$

We see now that the region of the allowed  $2\mathbf{k}_0$  is bounded by a sphere, the centre of which is shifted through the vector  $2\mu\mathbf{k}_1$  ( $1 - 2\mu$ ) relative to the origin of the  $\mathbf{k}_1$  vector. (This origin is taken as the origin of the co-ordinate system in  $\mathbf{k}$ -space). The location of this sphere relative to the origin of the  $\mathbf{k}_1$  vector is important. The origin can be either inside or outside of the sphere. It is also important whether the end of  $\mathbf{k}_1$  is inside or outside of the sphere. The location inside the sphere indicates that  $\mathbf{k}_2 = 0$  is possible. This means that the ionization can take place from the highest level of the valence band. It is easily seen from (8) that for the energy of the primary electron considered here, namely  $J \leq E(\mathbf{k}_1) \leq 2J$  the ionization from the highest level is impossible. In our case the end of the  $\mathbf{k}_1$  vector is always situated outside of the sphere.

The following cases may occur:

I. Shown in Fig. 1.

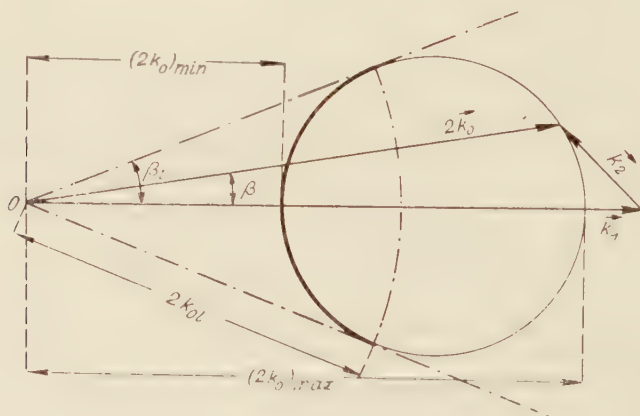


Fig. 1

It takes place for the following  $\mu$  and  $\mathbf{k}_1$ :

$$0 \leq \mu < \frac{1}{2} \quad \bar{k}_1^2 \leq k_1^2 \leq \bar{J}/(1 - \mu)$$

$$\mu \geq \frac{1}{2} \quad \bar{k}_1^2 \leq k_1^2 \leq 2\bar{J}.$$

Here  $\bar{J} = \frac{2m}{\hbar^2} J$ .

For the magnitude of  $2\mathbf{k}_0$  we have the following analytical expressions

$$\begin{aligned} 2k_{0\pm}(\beta) &= \frac{2\mu}{2\mu+1} \left\{ k_1 \cos \beta \pm \sqrt{k_1^2 \cos^2 \beta + \frac{1+2\mu}{2\mu^2} [k_1^2 (1-\mu) - \bar{J}]} \right\} \\ &= \frac{2\mu}{1+2\mu} k_1 \{ \cos \beta \pm \sqrt{\cos^2 \beta - \cos^2 \beta_I} \}. \end{aligned} \quad (10)$$

The angle  $\beta$  varies here from 0 to  $\beta_I$  and  $2k_{0\pm}$  refer to the two parts of the sphere indicated in Fig. 1.

$$\cos^2 \beta_I = \frac{1+2\mu}{2\mu^2} \cdot \frac{1}{k_1^2} [\bar{J} - (1-\mu) k_1^2]. \quad (11)$$

The minimum value of  $|2\mathbf{k}_0|$  on the sphere is attained for  $\beta = 0$  and equals  $2k_{0-}(\beta = 0)$

$$(2k_0)_{\min} = \frac{2\mu}{1+2\mu} k_1 (1 - \sqrt{1 - \cos^2 \beta_I}), \quad (12a)$$

and the maximum value is  $2k_{0+}(\beta = 0)$

$$(2k_0)_{\max} = \frac{2\mu}{1+2\mu} k_1 (1 + \sqrt{1 - \cos^2 \beta_I}). \quad (12b)$$

$2k_{0I}$  is the value of  $|2\mathbf{k}_0|$  at  $\beta = \beta_I$ .

$$2k_{0I} = \frac{2\mu}{1+2\mu} k_1 \cos \beta_I. \quad (13)$$

II. Shown in Fig. 2.

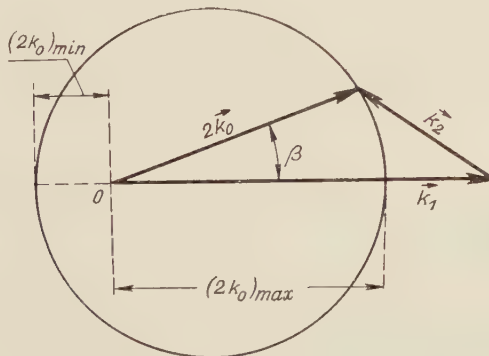


Fig. 2

Case II occurs for  $\mu < \frac{1}{2}$  and  $\bar{J}/(1-\mu) < k_1^2 \leq 2\bar{J}$ .

For  $2\mathbf{k}_0$  we have the following analytical expressions

$$2k_{0,0}(\beta) = \frac{2\mu}{1+2\mu} \left\{ k_1 \cos \beta + \sqrt{k_1^2 \cos^2 \beta + \frac{1+2\mu}{2\mu^2} [k_1^2 (1-\mu) - \bar{J}]} \right\}$$

$$= \frac{2\mu}{1+2\mu} k_1 \{ \cos \beta + \sqrt{\cos^2 \beta + \gamma^2} \}, \quad (14)$$

$$\gamma^2 = \frac{1+2\mu}{2\mu^2} \cdot \frac{1}{k_1^2} [k_1^2 (1-\mu) - J]. \quad (15)$$

Here the angle  $\beta$  varies from 0 to  $\pi$ .

The minimum value of  $|2\mathbf{k}_0|$  on the surface of the sphere is attained at  $\beta = \pi$

$$(2k_0)_{\min} = \frac{2\mu}{1+2\mu} k_1 (-1 + \sqrt{1 + \gamma^2}), \quad (16a)$$

and the maximum value is at  $\beta = 0$

$$(2k_0)_{\max} = \frac{2\mu}{1+2\mu} k_1 (1 + \sqrt{1 + \gamma^2}). \quad (16b)$$

We now look for the region circumscribed by the ends of the vector  $(\mathbf{k}'_1 + \mathbf{k}'_2)$  taking into account only the law of conservation of energy. The primary electron can ionize the electrons from different allowed energy levels in the valence band. Hence the total possible energy of this pair of electrons before the ionization process

$$\mathcal{E} = E(\mathbf{k}_1) + E(\mathbf{k}_2)$$

changes its value according to the energy level from which the electron is ionized.

$$\mathcal{E}_{\min} \leq \mathcal{E} \leq \mathcal{E}_{\max},$$

where

$$\begin{aligned} \mathcal{E}_{\max} &= E(\mathbf{k}_1) + E_{\max}(\mathbf{k}_2) = E(\mathbf{k}_1) + E(|\mathbf{k}_2|_{\min}) \\ &= \frac{\hbar^2}{m} (k_0)_{\max}^2, \end{aligned} \quad (17a)$$

$$\begin{aligned} \mathcal{E}_{\min} &= E(\mathbf{k}_1) + E_{\min}(\mathbf{k}_2) = E(\mathbf{k}_1) + E(|\mathbf{k}_2|_{\max}) \\ &= \frac{\hbar^2}{m} (k_0)_{\min}^2, \end{aligned} \quad (17b)$$

and  $(2k_0)_{\max}$ ,  $(2k_0)_{\min}$  are given by (12a,b) and (16a,b). In the further calculations we shall put  $\bar{\mathcal{E}} = \frac{2m}{\hbar^2} \mathcal{E}$ .

In order to fulfill the law of conservation of energy in the ionization process the vectors  $\mathbf{k}'_1$  and  $\mathbf{k}'_2$  must be such that

$$\mathcal{E}_{\min} \leq E(\mathbf{k}'_1) + E(\mathbf{k}'_2) \leq \mathcal{E}_{\max} \quad (18)$$

Since the ionization is possible from different energy levels in the valence band, we can have for a fixed  $E(\mathbf{k}'_1)$  such  $E(\mathbf{k}'_2)$  that the relation (18) is satisfied.

$$\begin{aligned} E(\mathbf{k}'_1) &\text{ can vary from 0 to } \mathcal{E}_{\max}. \text{ At } E(\mathbf{k}'_1) = 0, \\ \mathcal{E}_{\max} &\geq E(\mathbf{k}'_2) \geq \mathcal{E}_{\min}, \text{ at } E(\mathbf{k}'_1) = \mathcal{E}_{\max}, E(\mathbf{k}'_2) = 0. \end{aligned}$$

The region circumscribed by the vectors  $(\mathbf{k}'_1 + \mathbf{k}'_2)$  can be easily found from the relation (18). The following situations take place:

$$1. \ 0 \leq E(\mathbf{k}'_1) \leq \frac{1}{2} \mathcal{E}_{\min}.$$

The ends of  $(\mathbf{k}'_1 + \mathbf{k}'_2)$  give an excavated sphere with

$$\begin{aligned} \text{internal radius } r_{\min} &= \sqrt{\mathcal{E}_{\min} - k_1'^2} - k_1', \\ \text{external radius } R_{\max} &= \sqrt{\mathcal{E}_{\max} - k_1'^2} + k_1'. \end{aligned}$$

$$2. \ \frac{1}{2} \mathcal{E}_{\min} \leq E(\mathbf{k}'_1) \leq \frac{1}{2} \mathcal{E}_{\max}.$$

The ends of  $(\mathbf{k}'_1 + \mathbf{k}'_2)$  give a sphere with the radius

$$R_{\max} = \sqrt{\mathcal{E}_{\max} - k_1'^2} + k_1'.$$

$$3. \ \frac{1}{2} \mathcal{E}_{\max} \leq E(\mathbf{k}_1) \leq \mathcal{E}_{\max}.$$

The ends of  $(\mathbf{k}'_1 + \mathbf{k}'_2)$  give an excavated sphere with

$$\begin{aligned} \text{internal radius } R_{\min} &= k_1' - \sqrt{\mathcal{E}_{\max} - k_1'^2}, \\ \text{external radius } R_{\max} &= k_1' + \sqrt{\mathcal{E}_{\max} - k_1'^2}. \end{aligned}$$

Since the vectors  $(\mathbf{k}'_1 + \mathbf{k}'_2)$  must simultaneously fulfill the law of conservation of momentum  $\mathbf{k}'_1 + \mathbf{k}'_2 = 2\mathbf{k}_0$ , the region of integration for fixed  $E(\mathbf{k}'_1)$  is given as a common part of the spheres discussed above and the sphere of allowed  $2\mathbf{k}_0$ .

The integral in expression (6) can now be evaluated. A more detailed discussion reveals that the regions of integration depend on the values of the ratio  $\mathcal{E}_{\min}/\mathcal{E}_{\max}$ . This ratio is a function of  $\mu$  and  $\mathbf{k}_1$ .

We consider first the regions of integration for the 1st case above. There are four different limits  $\mathcal{E}_{\min}/\mathcal{E}_{\max}$  in which the integration regions are different.

$$\frac{1}{2} < \mathcal{E}_{\min}/\mathcal{E}_{\max} \leq 1 \quad (\text{I.1})$$

$$\frac{1}{2} (3 - \sqrt{5}) < \mathcal{E}_{\min}/\mathcal{E}_{\max} \leq \frac{1}{2} \quad (\text{I.2})$$

$$\frac{1}{4} < \mathcal{E}_{\min}/\mathcal{E}_{\max} \leq \frac{1}{2} (3 - \sqrt{5}) \quad (\text{I.3})$$

$$0 \leq \mathcal{E}_{\min}/\mathcal{E}_{\max} \leq \frac{1}{4} \quad (\text{I.4})$$

Now we enumerate for what values of  $\mu$  and  $\mathbf{k}_1$  the  $\mathcal{E}_{\min}/\mathcal{E}_{\max}$  lie in the specified ranges. These ranges are determined by the characteristic parameters, that is the values of  $\mathbf{k}_1$  for which

$$\mathcal{E}_{\min}/\mathcal{E}_{\max} = \frac{1}{2}, \frac{1}{2} (3 - \sqrt{5}), \frac{1}{4}.$$

$$\mathcal{E}_{\min}/\mathcal{E}_{\max} = \frac{1}{2} \text{ for}$$

$$\kappa_1^2 = \kappa_1^2 = \frac{1 + 2\mu}{1 + \mu - 2\mu^2 (\sqrt{2} - 1)^4} \bar{J},$$

$$\mathcal{O}_{\min}/\mathcal{O}_{\max} = \frac{1}{2} (3 - \sqrt{5}) \text{ for}$$

$$k_1^2 = \kappa_2^2 = \frac{1 + 2\mu}{1 + \mu - 2\mu^2 (\sqrt{5} - 2)^2} \bar{J},$$

$$\mathcal{O}_{\min}/\mathcal{O}_{\max} = \frac{1}{4} \text{ for}$$

$$k_1^2 = \kappa_3^2 = \frac{1 + 2\mu}{1 + \mu - 2\mu^2 \cdot \frac{1}{9}} \bar{J}.$$

Notice that  $\kappa_1^2 < \kappa_2^2 < \kappa_3^2$ .

We can now write down the values of  $\mu$  and  $k_1$  for different ratios  $\mathcal{O}_{\min}/\mathcal{O}_{\max}$  and therefore different regions of integration.

$$0 \leq \mu < \frac{1}{2}$$

$$\bar{k}_1^2 \leq k_1^2 < \kappa_1^2 \quad \frac{1}{2} < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq 1$$

$$\kappa_1^2 \leq k_1^2 < \kappa_2^2 \quad \frac{1}{2} (3 - \sqrt{5}) < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq \frac{1}{2}$$

$$\kappa_2^2 \leq k_1^2 < \kappa_3^2 \quad \frac{1}{4} < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq \frac{1}{2} (3 - \sqrt{5})$$

$$\kappa_3^2 \leq k_1^2 \leq \bar{J}/(1 - \mu) \quad 0 \leq \mathcal{O}_{\min}/\mathcal{O}_{\max} < \frac{1}{4}$$

$$\frac{1}{2} \leq \mu < \frac{3}{2}$$

$$\bar{k}_1^2 \leq k_1^2 < \kappa_1^2 \quad \frac{1}{2} < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq 1$$

$$\kappa_1^2 \leq k_1^2 < \kappa_2^2 \quad \frac{1}{2} (3 - \sqrt{5}) < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq \frac{1}{2}$$

$$\kappa_2^2 \leq k_1^2 < \kappa_3^2 \quad \frac{1}{4} < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq \frac{1}{2} (3 - \sqrt{5})$$

$$\kappa_3^2 \leq k_1^2 \leq 2\bar{J} \quad 0 < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq \frac{1}{4}$$

$$\frac{3}{2} \leq \mu < 1 + \frac{1}{2}\sqrt{5} \approx 2.118$$

$$\bar{k}_1^2 \leq k_1^2 < \kappa_1^2 \quad \frac{1}{2} < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq 1$$

$$\kappa_1^2 \leq k_1^2 < \kappa_2^2 \quad \frac{1}{2} (3 - \sqrt{5}) < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq \frac{1}{2}$$

$$\kappa_2^2 \leq k_1^2 \leq 2\bar{J} \quad \frac{1}{4} < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq \frac{1}{2} (3 - \sqrt{5})$$

$$1 + \frac{1}{2}\sqrt{5} \leq \mu < \frac{3}{2} + \sqrt{2} \approx 2.91$$

$$\bar{k}_1^2 \leq k_1^2 < \kappa_1^2 \quad \frac{1}{2} < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq 1$$

$$\kappa_1^2 \leq k_1^2 \leq 2\bar{J} \quad \frac{1}{2} (3 - \sqrt{5}) < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq \frac{1}{2}$$

$$\frac{3}{2} + \sqrt{2} \leq \mu < \infty$$

$$\bar{k}_1^2 \leq k_1^2 \leq 2\bar{J} \quad \frac{1}{2} < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq 1$$

In the second case there are two different limits  $\mathcal{O}_{\min}/\mathcal{O}_{\max}$  in which the regions of integration are different:

$$\frac{1}{2} < \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq 1 \quad (\text{II.1})$$

$$0 \leq \mathcal{O}_{\min}/\mathcal{O}_{\max} \leq \frac{1}{2} \quad (\text{II.2})$$



Here  $\mathcal{E}_{\min}/\mathcal{E}_{\max} = \frac{1}{2}$  for

$$k_1^2 = \kappa_4^2 = \frac{1 + 2\mu}{1 + \mu - 2\mu^2 (1 + \sqrt{2})^4} \bar{J}.$$

We can now write down the values of  $\mu$  and  $k_1$  for the different ratios  $\mathcal{E}_{\min}/\mathcal{E}_{\max}$ .

$$0 \leq \mu < \frac{3}{2} - \sqrt{2} \approx 0.0858$$

$$\bar{J}/(1 - \mu) < k_1^2 < \kappa_4^2$$

$$0 \leq \mathcal{E}_{\min}/\mathcal{E}_{\max} < \frac{1}{2}$$

$$\kappa_4^2 \leq k_1^2 \leq 2\bar{J}$$

$$\frac{1}{2} \leq \mathcal{E}_{\min}/\mathcal{E}_{\max} \leq 1$$

$$\frac{3}{2} - \sqrt{2} \leq \mu < \frac{1}{2}$$

$$\bar{J}/(1 - \mu) < k_1^2 \leq 2\bar{J}$$

$$0 \leq \mathcal{E}_{\min}/\mathcal{E}_{\max} < \frac{1}{2}.$$

The determination of the integration regions is shown in detail in Fig. 3 for the particular case (I.1). There we exhibit the dependence of  $R_{\max}$ ,  $R_{\min}$  and  $r_{\min}$  on

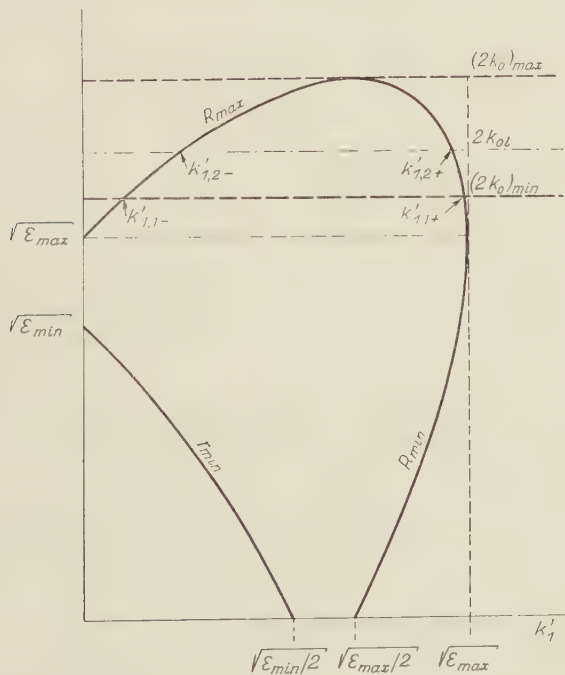


Fig. 3

$k'_1$  and the situation of the curves  $R_{\max}(k'_1)$ ,  $R_{\min}(k'_1)$  and  $r_{\min}(k'_1)$  relative to the sphere of the allowed  $2k_0$ . The figure exhibits only the magnitude of the vector  $2k_0$  without taking into account the angle  $\beta$ .

We can find from the figure the values of  $k'_1$  for which  $R_{\max}(k'_1) < (2k_0)_{\min}$ , that is the spheres considered have no common region. Let us denote by  $k'_{1,1-}$  and

$k'_{1,1+}$  the points of intersection of the curve  $R_{\max}(\mathbf{k}'_1)$  with the line  $(2k_0)_{\min}$ . We notice at once that for the values of  $k'_1$  in the intervals

$$0 \leq k'_1 \leq k'_{1,1-} \text{ and } k'_{1,1+} \leq k'_1 \leq \sqrt{\overline{\mathcal{E}_{\max}}}$$

the region of the  $\mathbf{k}_0$  integration is zero. Therefore for these values of  $k'_1$  the probability function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  vanishes.

The values of  $k'_{1,1\pm}$  are given by

$$k'_{1,1\pm} = \frac{1}{\sqrt{2}} (\sqrt{\overline{\mathcal{E}_{\min}}} \pm \sqrt{\overline{\mathcal{E}_{\max}} - \overline{\mathcal{E}_{\min}}})$$

In Fig. 4 the  $\mathbf{k}_0$  integration region is shown for the case  $(2k_0)_{\min} < R_{\max}(\mathbf{k}'_1) < 2k_{0l}$ . Considering Fig. 3 and denoting there by  $k'_{1,2+}$ ,  $k'_{1,2-}$  the intersection points of the curve  $R_{\max}(\mathbf{k}'_1)$  with the line  $2k_{0l}$ , we see that the integration region of the shape

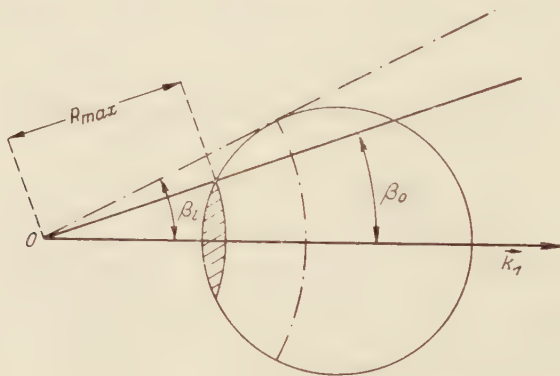


Fig. 4

shown in Fig. 4 appears if the  $k'_1$  values lie in the intervals  $k'_{1,1-} \leq k'_1 \leq k'_{1,2-}$  and  $k'_{1,2+} \leq k'_1 \leq k'_{1,1+}$ . The values of  $k'_{1,2\pm}$  are given by

$$k'_{1,2\pm} = \frac{1}{\sqrt{2}} (\sqrt{\overline{\mathcal{E}_l}} \pm \sqrt{\overline{\mathcal{E}_{\max}} - \overline{\mathcal{E}_l}}), \text{ where } \overline{\mathcal{E}_l} = \sqrt{\overline{\mathcal{E}_{\max}} \cdot \overline{\mathcal{E}_{\min}}}.$$

The integration limits resulting from Fig. 4 are

$$0 \leq \beta < \beta_0, \quad 2k_{0-} \leq 2k_0 \leq R_{\max}.$$

The angle  $\beta_0$  depends on  $\mathbf{k}'_1$ . The  $\cos \beta_0$  is obtained from the equation  $2k_{0-}(\beta_0) = R_{\max}(\mathbf{k}'_1)$  as

$$\cos \beta_0 = \frac{\mu}{1 + 2\mu} \cdot \frac{1}{k_1 R_{\max}} \left[ \left( \frac{1 + 2\mu}{2\mu} \right)^2 R_{\max}^2 + k_1^2 \cos^2 \beta_l \right]. \quad (19)$$

In Fig. 3 we have still to consider the interval of the  $k'_1$  values  $k'_{1,2-} \leq k'_1 \leq k'_{1,2+}$ . In this interval  $R_{\max}(\mathbf{k}'_1) > 2k_{0l}$  and it attains its maximal value  $R_{\max} = (2k_0)_{\max}$ .

at  $k'_1 = \sqrt{\bar{\mathcal{E}}_{\max}/2}$ . The region of the  $\mathbf{k}_0$  integration for this interval of  $k'_1$  is shown in Fig. 5

We have here the following limits of integration for  $\beta$  and  $2k_0$

$$\begin{aligned} 0 &\leq \beta \leq \beta_1 & 2k_{0-} &\leq 2k_0 \leq R_{\max} \\ \beta_1 &\leq \beta \leq \beta_l & 2k_{0-} &\leq 2k_0 \leq 2k_{0+}. \end{aligned}$$

The angle  $\beta_1$  is obtained from the equation  $2k_{0+}(\beta_1) = R_{\max}(\mathbf{k}'_1)$  and is given by expression identical with (19).

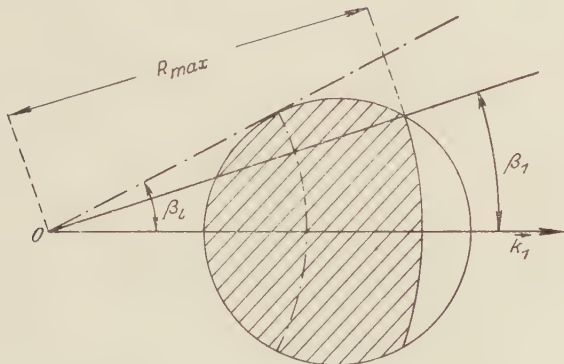


Fig. 5

In an analogical way, using figures similar to Fig. 3,4,5, we can determine explicitly the regions of the  $\mathbf{k}_0$  integration for the other cases.

Performing the integration for all these cases the expressions for the function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  are obtained.

Let us now collect all the characteristic values appearing in the determination of the regions of the  $\mathbf{k}_0$  integration for all the cases:

$$\begin{aligned} k'_{1,\pm} &= \frac{1}{\sqrt{2}} (\sqrt{\bar{\mathcal{E}}_{\min}} \pm \sqrt{\bar{\mathcal{E}}_{\max} - \bar{\mathcal{E}}_{\min}}), \\ k'_{1,2\pm} &= \frac{1}{\sqrt{2}} (\sqrt{\bar{\mathcal{E}}_l} \pm \sqrt{\bar{\mathcal{E}}_{\max} - \bar{\mathcal{E}}_l}), \\ k'_{1,3} &= \sqrt{\bar{\mathcal{E}}_{\max}/2 + \bar{\mathcal{E}}_l}. \end{aligned}$$

For the I-st case

$$\cos \beta_0 = \cos \beta_1 = \frac{\mu}{1+2\mu} \cdot \frac{1}{k_1 R_{\max}} \left[ \left( \frac{1+2\mu}{2\mu} \right)^2 R_{\max}^2 + k_1^2 \cos^2 \beta_l \right].$$

$\cos \beta_0$  is obtained from the relation  $R_{\max} = 2k_{0-}(\beta_0)$  and

$\cos \beta_1$  from the relation  $R_{\max} = 2k_{0+}(\beta_1)$ .

$$\cos \beta_2 = \cos \beta_3 = \frac{\mu}{1+2\mu} \cdot \frac{1}{k_1 R_{\min}} \left[ \left( \frac{1+2\mu}{2\mu} \right)^2 R_{\min}^2 + k_1^2 \cos^2 \beta_l \right].$$

$\cos \beta_2$  is obtained from the relation  $R_{\min} = 2k_{0-}(\beta_2)$  and  $\cos \beta_3$  from the relation  $R_{\min} = 2k_{0+}(\beta_3)$ .

In the case II we have in place of  $\cos^2 \beta_l$  the quantity  $(-\gamma^2)$  in the expressions for  $\cos \beta_0$  and  $\cos \beta_2$ .

Let us now write down the function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  for all the cases mentioned above.

Intervals of $k'_1$	$P(\mathbf{k}_1, E(\mathbf{k}'_1))$	
$(0, k'_{1,1-})$	0	(I.1)
$(k'_{1,1-}, k'_{1,2-})$	$C A_1(R_{\max}, \cos \beta_0)$	
$(k'_{1,2-}, k'_{1,2+})$	$C[A_1(R_{\max}, \cos \beta_1) + A_2(\cos \beta_1)]$	
$(k'_{1,2+}, k'_{1,1+})$	$C A_1(R_{\max}, \cos \beta_0)$	
$(k'_{1,1+}, \sqrt{\mathcal{E}_{\max}})$	0	
$(0, k'_{1,2-})$	$C A_1(R_{\max}, \cos \beta_0)$	(I.2)
$(k'_{1,2-}, k'_{1,2+})$	$C[A_1(R_{\max}, \cos \beta_1) + A_2(\cos \beta_1)]$	
$(k'_{1,2+}, k'_{1,1+})$	$C A_1(R_{\max}, \cos \beta_0)$	
$(k'_{1,1+}, \sqrt{\mathcal{E}_{\max}})$	$C[A_3(R_{\max}, R_{\min}, \cos \beta_2) + A_4(R_{\max}, \cos \beta_0, \cos \beta_2)]$	
$(0, k'_{1,2-})$	$C A_1(R_{\max}, \cos \beta_0)$	(I.3)
$(k'_{1,2-}, k'_{1,1+})$	$C[A_1(R_{\max}, \cos \beta_1) + A_2(\cos \beta_1)]$	
$(k'_{1,1+}, k'_{1,2+})$	$C[A_2(\cos \beta_1) + A_3(R_{\max}, R_{\min}, \cos \beta_2) +$ $+ A_4(R_{\max}, \cos \beta_1, \cos \beta_2)]$	
$(k'_{1,2+}, \sqrt{\mathcal{E}_{\max}})$	$C[A_3(R_{\max}, R_{\min}, \cos \beta_2) + A_4(R_{\max}, \cos \beta_0, \cos \beta_2)]$	
$(0, k'_{1,1+})$	$C[A_1(R_{\max}, \cos \beta_1) + A_2(\cos \beta_1)]$	(I.4)
$(k'_{1,1+}, k'_{1,3})$	$C[A_2(\cos \beta_1) + A_3(R_{\max}, R_{\min}, \cos \beta_2) +$ $+ A_4(R_{\max}, \cos \beta_1, \cos \beta_2)]$	
$(k'_{1,3}, k'_{1,2+})$	$C[A_2(\cos \beta_2) + A_3(R_{\max}, R_{\min}, \cos \beta_1) +$ $+ A_5(R_{\min}, \cos \beta_1, \cos \beta_2)]$	
$(k'_{1,2+}, \sqrt{\mathcal{E}_{\max}})$	$C[A_3(R_{\max}, R_{\min}, \cos \beta_1) + A_5(R_{\min}, \cos \beta_1, \cos \beta_3)]$	
$(0, \sqrt{\mathcal{E}_{\min}/2})$	$C[B_1(R_{\max}, r_{\min}, \cos \beta_0) + B_2(r_{\min}, \cos \beta_0)]$	(II.1)
$(\sqrt{\mathcal{E}_{\min}/2}, \sqrt{\mathcal{E}_{\max}/2})$	$C[B_3(R_{\max}, \cos \beta_0) + B_4(\cos \beta_0)]$	
$(\sqrt{\mathcal{E}_{\max}/2}, k'_{1,1+})$	$C[B_1(R_{\max}, R_{\min}, \cos \beta_0) + B_2(R_{\min}, \cos \beta_0)]$	
$(k'_{1,1+}, \sqrt{\mathcal{E}_{\max}})$	$C[B_1(R_{\max}, R_{\min}, \cos \beta_0) + B_5(R_{\min}, \cos \beta_0, \cos \beta_2)]$	

$$\begin{array}{ll}
(0, k'_{1,1-}) & C.B_6 (R_{\max}, r_{\min}) \\
(k'_{1,1-}, \sqrt{\mathcal{E}_{\min}/2}) & C[B_1 (R_{\max}, r_{\min}, \cos \beta_0) + B_2 (r_{\min}, \cos \beta_0)] \\
(\sqrt{\mathcal{E}_{\min}/2}, \sqrt{\mathcal{E}_{\max}/2}) & C[B_3 (R_{\max}, \cos \beta_0) + B_4 (\cos \beta_0)] \\
(\sqrt{\mathcal{E}_{\max}/2}, k'_{1,1+}) & C[B_1 (R_{\max}, R_{\min}, \cos \beta_0) + B_2 (R_{\min}, \cos \beta_0)] \\
(k'_{1,1+}, \sqrt{\mathcal{E}_{\max}}) & C.B_6 (R_{\max}, R_{\min})
\end{array} \tag{II.2}$$


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The functions  $A_j$  and  $B_j$  are given in the following forms:

$$\begin{aligned}
A_1 (R_{\max}, \cos \beta_0) = \pi \left\{ \frac{1}{4} R_{\max}^2 (1 - \cos \beta_0) - \left( \frac{\mu}{1 + 2\mu} \right)^2 k_1^2 \left[ \frac{2}{3} (1 - \cos^3 \beta_0) - \right. \right. \\
\left. \left. - \cos^2 \beta_l (1 - \cos \beta_0) - \frac{2}{3} \sqrt{(1 - \cos^2 \beta_l)^3} + \frac{2}{3} \sqrt{(\cos^2 \beta_0 - \cos^2 \beta_l)^3} \right] \right\},
\end{aligned}$$

$$A_2 (\cos \beta_1) = \frac{4}{3} \pi \left( \frac{\mu}{1 + 2\mu} \right)^2 k_1^2 \sqrt{(\cos^2 \beta_1 - \cos^2 \beta_l)^3},$$

$$A_3 (R_{\max}, R_{\min}, \cos \beta_2) = \frac{\pi}{4} (R_{\max}^2 - R_{\min}^2) (1 - \cos \beta_2)$$

$$\begin{aligned}
A_4 (R_{\max}, \cos \beta_1, \cos \beta_2) = \pi \left\{ \frac{1}{4} R_{\max}^2 (\cos \beta_2 - \cos \beta_1) - \left( \frac{\mu}{1 + 2\mu} \right)^2 k_1^2 \times \right. \\
\times \left[ \frac{2}{3} (\cos^3 \beta_2 - \cos^3 \beta_1) - \cos^2 \beta_l (\cos \beta_2 - \cos \beta_1) - \right. \\
\left. \left. - \frac{2}{3} \sqrt{(\cos^2 \beta_2 - \cos^2 \beta_l)^3} + \frac{2}{3} \sqrt{(\cos^2 \beta_1 - \cos^2 \beta_l)^3} \right] \right\}
\end{aligned}$$

$$\begin{aligned}
A_5 (R_{\min}, \cos \beta_1, \cos \beta_2) = \pi \left\{ \left( \frac{\mu}{1 + 2\mu} \right)^2 k_1^2 \left[ \frac{2}{3} (\cos^3 \beta_1 - \cos^3 \beta_2) - \right. \right. \\
\left. \left. - \cos^2 \beta_l (\cos \beta_1 - \cos \beta_2) + \frac{2}{3} \sqrt{(\cos^2 \beta_1 - \cos^2 \beta_l)^3} - \right. \right. \\
\left. \left. - \frac{2}{3} \sqrt{(\cos^2 \beta_2 - \cos^2 \beta_l)^3} \right] - \frac{1}{4} R_{\min}^2 (\cos \beta_1 - \cos \beta_2) \right\}
\end{aligned}$$

$$B_1 (R_{\max}, r_{\min}, \cos \beta_0) = \frac{\pi}{4} (R_{\max}^2 - r_{\min}^2) (1 - \cos \beta_0)$$

$$\begin{aligned}
B_2 (r_{\min}, \cos \beta_0) = \pi \left\{ \left( \frac{\mu}{1 + 2\mu} \right)^2 k_1^2 \left[ \frac{2}{3} (\cos^3 \beta_0 + 1) + \gamma^2 (\cos \beta_0 + 1) + \right. \right. \\
\left. \left. + \frac{2}{3} \sqrt{(\cos^2 \beta_0 + \gamma^2)^3} - \frac{2}{3} \sqrt{(1 + \gamma^2)^3} \right] - \frac{1}{4} r_{\min}^2 (\cos \beta_0 + 1) \right\}
\end{aligned}$$



$$\begin{aligned}
B_3(R_{\max}, \cos \beta_0) &= \pi \frac{1}{4} R_{\max}^2 (1 - \cos \beta_0) \\
B_4(\cos \beta_0) &= \pi \left( \frac{\mu}{1 + 2\mu} \right)^2 k_1^2 \left[ \frac{2}{3} (\cos^3 \beta_0 + 1) + \gamma^2 (\cos \beta_0 + 1) + \right. \\
&\quad \left. + \frac{2}{3} \sqrt{(\cos^2 \beta_0 + \gamma^2)^3} - \frac{2}{3} \sqrt{(1 + \gamma^2)^3} \right] \\
B_5(R_{\min}, \cos \beta_0, \cos \beta_2) &= \pi \left\{ \left( \frac{\mu}{1 + 2\mu} \right)^2 k_1^2 \left[ \frac{2}{3} \cos^3 \beta_0 - \cos^3 \beta_2 + \right. \right. \\
&\quad \left. + \gamma^2 (\cos \beta_0 - \cos \beta_2) + \frac{2}{3} \sqrt{(\cos^2 \beta_0 + \gamma^2)^3} - \right. \\
&\quad \left. \left. - \frac{2}{3} \sqrt{(\cos^2 \beta_2 + \gamma^2)^3} \right] - \frac{1}{4} R_{\min}^2 (\cos \beta_0 - \cos \beta_2) \right\} \\
B_6(R_{\max}, r_{\min}) &= \frac{1}{2} \pi (R_{\max}^2 - r_{\min}^2).
\end{aligned}$$

The character of the function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  was investigated in its dependence on  $E(\mathbf{k}'_1)$  for several parameters  $\mu$  and  $k_1$  which correspond to the different cases, of integration.

We get only three characteristic, qualitatively different, shapes of the function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$ , namely:

(1) The function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  is for some values of  $E(\mathbf{k}'_1)$  equal to zero. This case comes about for such  $\mu$  and  $k_1^2 \leq J_1(1 - \mu) \leq 2J_1$ , for which  $\frac{1}{2} \leq \mathcal{E}_{\min}' / \mathcal{E}_{\max}' < 1$ .

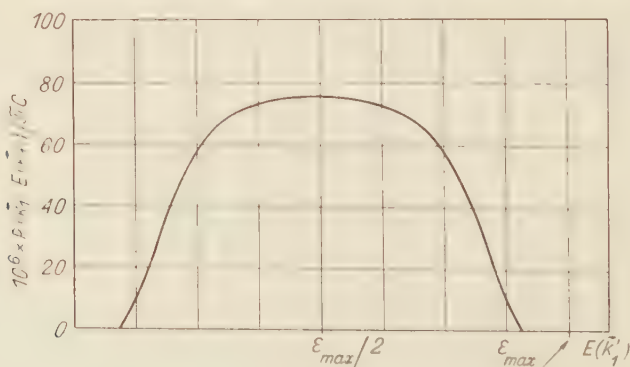


Fig. 6

$E(\mathbf{k}'_1)$  is confined to the interval  $(0, \mathcal{E}_{\max})$ . The function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  is symmetrical with respect to its maximum. It reaches the maximum for  $E(\mathbf{k}'_1) = \mathcal{E}_{\max}/2$ . An example of such a function is shown in Fig. 6. It has been computed for  $\mu = 2$ , and  $k_1 = 1.297 \sqrt{J_1}$ .

- (2) The function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  is equal to 0 only for  $E(\mathbf{k}'_1) = 0, \mathcal{E}_{\max}$ . It is a symmetrical function with a maximum at  $E(\mathbf{k}'_1) = \mathcal{E}_{\max}/2$ . This type of function is obtained for such  $\mu$  and  $k_1$ , for which  $\mathcal{E}_{\min}/\mathcal{E}_{\max} = \frac{1}{2}$ . An example computed for  $\mu = 2$  and  $k_1 = 1.3452 \sqrt{J}$  is shown in Fig. 7.

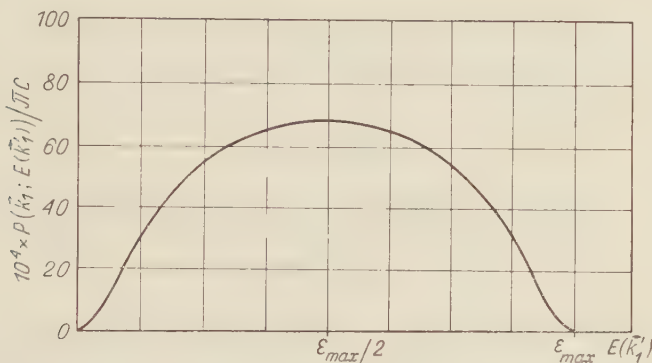


Fig. 7

- (3) The function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  has a definite value, different from zero for  $E(\mathbf{k}'_1) = 0$ . This case can be realized either for  $\mu$  and  $k_1^2 < \bar{J}/(1 - \mu) < 2\bar{J}$  such that  $\mathcal{E}_{\min}/\mathcal{E}_{\max} < \frac{1}{2}$  or for  $\mu < \frac{1}{2}$  and  $2\bar{J} > k_1^2 > \bar{J}/(1 - \mu)$ . The maximum of  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  is at  $E(\mathbf{k}'_1) = \mathcal{E}_{\max}/2$ . The function  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  depends only slightly on  $E(\mathbf{k}'_1)$  in the neighbourhood of the maximum. This means that the

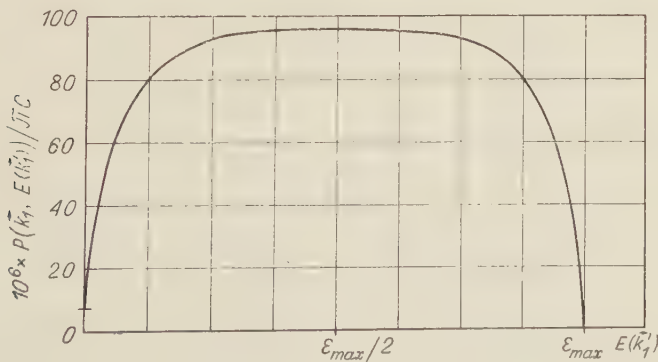


Fig. 8

probability is almost independent of  $E(\mathbf{k}'_1)$  about  $\mathcal{E}_{\max}/2$  though it depends on  $E(\mathbf{k}'_1)$  strongly about 0 and  $\mathcal{E}_{\max}$ .

Two examples computed for  $\mu = 0.1$  are shown in Fig. 8 for  $k_1 = 1.0449 \sqrt{J}$  and in Fig. 9 for  $k_1 = 1.0452 \sqrt{J}$ .

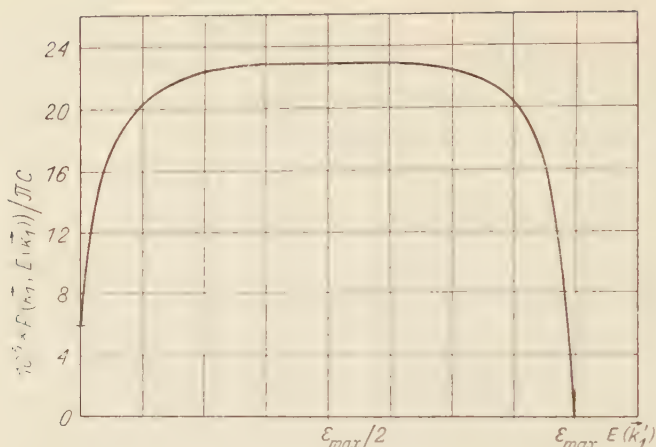


Fig. 9

The expression for  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  has been given in Franz's paper (1956) only in the case of a vanishing width of the valence band. In order to get Franz's result from our computations, we must take a properly defined interval of  $E(\mathbf{k}_1)$  and consider the limiting case  $\mu \rightarrow 0$ .

We have to consider the following limits for  $\mu$  and  $k_1$

$$0 \leq \mu < \frac{3}{2} - \sqrt{2}$$

$$\kappa_4^2 \leq k_1^2 \leq \bar{J}$$

When  $\mu \rightarrow 0$ ,  $\kappa_4^2 \rightarrow \bar{J}$  and  $k_1^2$  varies from  $\bar{J}$  to  $2\bar{J}$ . In order to give the expression for  $P(\mathbf{k}_1, E(\mathbf{k}'_1))$  for  $\mu = 0$  we must consider the case (II.2).

When  $\mu \rightarrow 0$ , then  $\mathcal{E}_{\max} = \mathcal{E}_{\min} = \mathcal{E} = E(\mathbf{k}_1) = J$ ,  $k_{1+}^2 = k_{1-}^2 = \bar{\mathcal{E}}/2$  and for all the values  $E(\mathbf{k}'_1)$  from 0 to  $\mathcal{E}$  we have

$$P(\mathbf{k}_1, E(\mathbf{k}'_1)) = C(\mu = 0) \cdot B_6(|R_{\max}|, |R_{\min}|) =$$

$$= \frac{4m^2 e^4}{\pi^2 \hbar^5} \cdot \frac{|a(-\mathbf{k}_1)|^2}{k_1^4} \cdot \frac{\pi}{2} (R_{\max}^2 - R_{\min}^2) =$$

$$= \frac{4m e^4}{\pi \hbar^3} \cdot |a(-\mathbf{k}_1)|^2 \cdot \frac{\sqrt{E(\mathbf{k}'_1) [E(\mathbf{k}_1) - J - E(\mathbf{k}'_1)]}}{E^2(\mathbf{k}_1)}.$$

This expression agrees with that given by Franz.

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NOTE ON THE EFFECTS DUE TO PULSE-DELAY PHENOMENA  
IN  $\text{CO}_2 + \text{CS}_2$  G.-M. COUNTERS

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The possibility of using  $\text{CO}_2$  as principal agent for filling G.-M. counters was proved by Brown and Miller (1947). Of many mixtures tested,  $\text{CO}_2$  containing an admixture of several % of  $\text{CS}_2$  yielded the most satisfactory results when used for filling counters. The latter then presented a plateau length of several hundred volts and a slope of the order of 0.5–2% throughout the range of 50–100 V above the threshold Mościcki (1958). When measuring the  $T_{1/2}$  of  $^{14}\text{C}$ , Hawkings et al. (1949) determined the yield of counters of the type considered, which they found to amount to 96.2% in a counter of a diameter of 1.167 cm and to 98% in one of a diameter of 6.998 cm.

However, it should be stated that  $T_{1/2}$  measurements carried out with these counters showed discrepancies, as compared with those of authors using other techniques, especially argon-alcohol filled counters.

Direct comparison of the number of counts from the same sample as obtained with  $\text{CO}_2 + \text{CS}_2$  counters and with argon-alcohol counters containing a small admixture of active  $\text{CO}_2$ , proved the former to present a yield of 80–85% of that of the latter type of counter. The reasons for this reduced yield remained unknown (Miller et al. 1950).

When investigating the use of  $\text{CO}_2 + \text{CS}_2$  counters in the  $^{14}\text{C}$  dating method, the author noticed that the number of pulses of the background depended evidently on the time of blocking of the anticoincidence system by pulses of the shielding. Observation proved the number of additional background pulses  $\Delta B$  to be given approximately by the distribution

$$\Delta B = 0.65 L e^{-0.72 \cdot 10^4 \tau (\text{min})} \quad (1)$$

with  $L$  denoting the total number of pulses appearing in the counter, and  $\tau$  (in minutes) the width of pulse of the a.c. channel. With respect to the low accuracy in the evaluation of the a.c. multivibrator gates width occurring in the investigation

and the scarce statistics available, the accuracy of the constants in eq. (1) was estimated to be about 20%.

The increase in number of background pulses when the a.c. pulse width underwent shortening was interpreted as resulting from a delay of pulses in the counter under consideration with respect to the moment of transition of the ionizing particle. A pulse delay effect was also observed to occur in similar counters by Crain and Griffin (1958).

In his paper (1958), the author stressed that this delay effect can serve for explaining the differences in the results of  $T_{1/2}$  measurements obtained with the  $\text{CO}_2 + \text{CS}_2$  counter.

It is the aim of the present paper to discuss the influence of the delay effect on the accuracy of the device used for measuring very weak  $^{14}\text{C}$  sources, and to attempt an evaluation of  $T_{1/2}$  from the measurements by Miller and Hawkings et al. taking into account the effective time of measurement in their experimental conditions as resulting from time distribution data for pulse delay from  $\text{CO}_2 + \text{CS}_2$  counters (Mościcki, Renk).

#### a) Low level counting

Let  $N_0$  and  $L_0$  denote the number of ionizing particles per unit time passing through the anticoincidence shield and the measuring counter, respectively. Moreover,  $L_0 = B_0 + L_{k0}$ , wherein the index  $k$  stands for the penetrating cosmic rays component, and  $B_0$  is the counter background due to radioactive impurities in the counter and surroundings. If the a.c. channel gate width is  $\tau$ , then the effective recording time is;

$$T_{\text{eff}} = \frac{1}{1 + N_0 \tau},$$

and the number of pulses of the a.c. shielding recorded

$$N = \frac{N_0}{1 + N_0 \tau}.$$

If the usual single channel recording devices are used, the effect of the background recorded will consist of the following three components:

1) Pulses  $B_0$  not occurring in the dead time of the device

$$B_1 = \frac{B_0}{1 + N_0 \tau} \quad (2)$$

2) Pulses due to particles of the hard cosmic rays component passing in coincidence with some pulses  $N_0$ , but falling outside the interval of blocking of the a.c.



device as a result of the delay effect. The number of such pulses amounts to

$$B_2 = \frac{L_{0k}}{1 + N_0 \tau} \Phi(\tau), \quad (2a)$$

wherein  $\Phi(\tau)$  is the probability of firing the counter after the time  $\tau$ .

- 3) Pulses due to particles of the  $L_{0k}$  component passing through the measuring counter when the a.c. system is blocked, at a moment  $0 \leq t \leq \tau$  subsequent to the front of the a.c. system gate, with delays exceeding  $\tau - t$ , ( $\tau$  denotes the gate length). The background due to these pulses will amount to

$$B_3 = \frac{N_0 \cdot L_{0k}}{1 + N_0 \tau} \int_0^\tau \Phi(\tau - t) dt. \quad (2b)$$

The joint background effect arises by summing of the foregoing effects. As proved by the results available, and especially by the excellent plateau of this kind of counters, the contribution of double and multiple pulses to the total background level is not essential. Thus, the total background measured per unit time will be

$$B = (1 + N_0 \tau)^{-1} \{B_0 + L_{0k} [\Phi(\tau) + N_0 \int_0^\tau \Phi(\tau - t) dt]\}. \quad (3)$$

Assuming a delay distribution law of the form  $\Phi(t) = ke^{-\lambda t}$ , the following expression is obtained for the increase in the number of background pulses ( $\Delta B$ ) due to the delay effect:

$$\Delta B = (1 + N_0 \tau)^{-1} k L_{0k} \left\{ \frac{N_0}{\lambda} + \left( 1 - \frac{N_0}{\lambda} \right) e^{-\lambda \tau} \right\}. \quad (4)$$

Putting e.g.  $N_0 = 10^3$  cpm,  $\tau = 8.3 \times 10^{-5}$  min,  $L_0 = 250$  cpm, we have, with  $k = 0.65$ ,  $\lambda = 0.7 \times 10^5 \text{ min}^{-1}$ ,  $\Delta B = 2.5$  cpm, whereas with  $\lambda = 0.4 \times 10^5 \text{ min}^{-1}$ ,  $k = 0.5$ , we have  $\Delta B = 7$  cpm.

Of course, an increase in background level occurring simultaneously with reducing the time of measurement due to the necessity of applying very long time delays of the a.c. shielding channel tends to diminish the accuracy and sensitivity of the measurement. A criterion for the accuracy of the measurement may be given by  $C^2 = S^2/B$  ( $S$  denotes the activity of the sample in cpm). In the case of a detector for which the blocking time of the device can be neglected,  $C_0^2 = S_0^2/B_0$ . For a detector with delayed pulses, in addition to the increase in  $B$  according to eq. (4), there is a decrease in the number of pulses from the sample investigated, so that  $S = S_0/(1 + N_0 \tau)$  and

$$\frac{C_0^2}{C^2} = f(N_0, L_0, \tau, \Phi(\tau)). \quad (5)$$

The shape of this function for  $B_0 = 10$ ,  $L_0 = 200$ ,  $N_0 = 10^3$ ,  $\lambda = 10^5$ ,  $k = 1$  (graph *a*) and  $\lambda = 5 \times 10^5 \text{ min}^{-1}$ ,  $k = 0.5$  (graph *b*) is shown in Fig. 1.

The possibility of restricting the harmful influence of the pulse delay depends upon the use of electronic circuits for blocking the channel of the measuring counter for a period  $\tau$  subsequent to the appearance of each pulse of the a. c. shield<sup>1)</sup>.

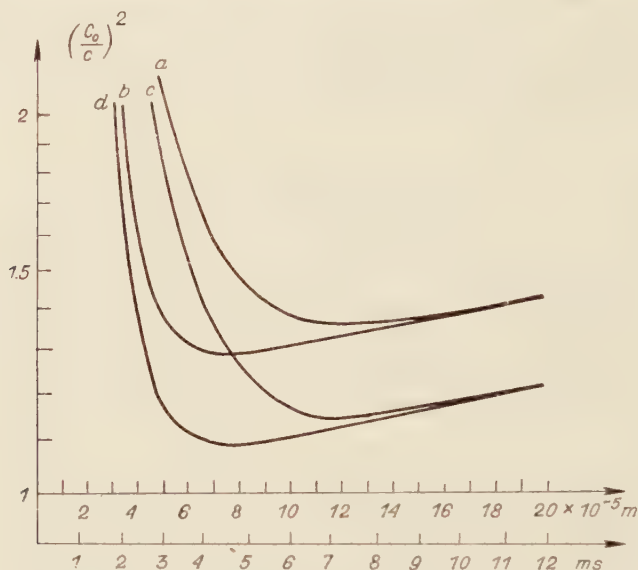


Fig. 1

In this case, the effective time of the measurement is being shorted and is satisfactorily approximated by the following expression:

$$T'_{\text{eff}} = \frac{1 - \left(\frac{N_0 \tau}{2}\right)^2}{1 + N_0}$$

However, if a circuit of this kind is used, practically all the pulses  $L_{k0}$  appearing with a delay lesser than  $\tau$  undergo quenching in the a.c. system.

Here, too, three sources contribute to the background effect. These are:

- 1) the background recorded during the effective time of the measurement,
- 2) pulses delayed by more than  $\tau$ ,
- 3) pulses delayed by more than  $\tau + t$  (where  $t < \tau$  is the a.c. gate length).

<sup>1)</sup> Indeed, such a device was applied with good results by Crane and Griffin. As these authors give no details, it may be useful to point out the following possibility. The pulses from the pre-amplifier of the a.c. shield trigger a bistable univibrator of appropriately chosen time delay, distributing the pulses over two identical channels. The pulses from either channel superpose in the summation circuit, yielding a pulse at the output lasting from  $\tau$  to  $2\tau$  according to the degree of superposition of the pulses coming from both channels.

Neglecting highly improbable cases of more than two pulses occurring within the interval  $\tau$ , the total background is now given by the following expression:

$$B' = B_0 T_{\text{eff}} + L_{0k} (1 + N_0 \tau)^{-1} \{ \Phi(\tau) + N_0 \int_0^\tau \Phi(\tau + t) dt \}. \quad (6)$$

Fig. 1 (graphs *c, d*) shows the dependence of the ratio  $C_0^2/C^2$  on  $\tau$ , with assumptions similar to those made previously.

#### b) $T_{1/2}$ $^{14}\text{C}$ measurements

Available  $T_{1/2}$   $^{14}\text{C}$  measurements include a group of results obtained with a  $\text{CO}_2 + \text{CS}_2$  counter working in the G.-M. region. The latter results differ obviously from those obtained by other methods<sup>2)</sup>. They are, however, consistent in yielding  $T_{1/2}$  values ranging from 6300 to 6100 years. As the respective authors do not take into consideration the pulse delay effect in counters of this type and the related dead time, it is of interest to investigate the corrections resulting from this effect relating to measurements by the technique considered.  $T_{1/2}$  measurements are characterized by a relatively high number of countings, amounting to several thousands cpm. In these conditions, the dead time of the counter is quite apparent and affects essentially the  $T_{1/2}$  results. Two of the published available, papers bring material that is adapted for checking, namely, those by Miller and Hawkings et al.

In computing the corrections, the delays distribution was assumed to be of the form

$$\Phi(t) = e^{-\lambda t}, \quad \text{with} \quad \lambda = 5 \times 10^4 \text{ mm}^{-1}. \quad (7)$$

The value of  $\lambda = 5 \times 10^4$  represents a compromise between the value of  $4.2 \times 10^4$  obtained by direct measurement and that of  $5.1 \times 10^4$  resulting from the discussion of the data obtained by the author with an M2 counter and taking into consideration the dependence of the background on the a.c. channel delay time (Mościcki and Renk 1960).

In Table I, the data published by Miller and the results obtained with the effective measurement time correction are assembled. The columns contain: 1 — the number denoting the counter in Miller's paper, 2 —  $N$  — the number of cpm measured in that paper, 3 —  $N_0$ , the number of cpm corrected with respect to the function  $\Phi(t)$ , 4 — the activity of the sample, 5 —  $f_c = N_0/N$ , 6 —  $f$  — the linearity correction factor given by Miller, 7 —  $f_0/f$ .

Columns 8 and 9 bring the values of the specific activities as obtained by Miller, account being taken of the linearity correction factor and the activity in cpm/mol with the correction for the dead time of the counter.

It is to be regretted that Miller does not give the method used in computing the linearity correction factor. It seems, however, that his method of determining the factor involved systematic error amounting to a coefficient of about 1.037. The dispersion of the ratio  $f_0/f$  in column 7 of Table I is, in fact, small. There is only

<sup>2)</sup> For tabellarized results, see e.g. Libby (1952)

Table I

Nr	N	N <sub>0</sub>	N <sub>0</sub> - T	$f_c = \frac{N_0}{N}$	f	f <sub>0</sub> /f	A Miller	A corr.
1	2	3	4	5	6	7	8	9
18	2090	2151	1861	1.043	1.000	1.043	44.0	46.2
19	1420	1462	1422	1.030	1.000	1.030	51.0	52.5
20	2200	2301	2222	1.046	1.005	1.041	47.3	49.1
23	5230	5841	5682	1.117	1.065	1.048	47.3	49.8
22	7130	8316	8217	1.166	1.138	1.025	46.3	47.6
18	9840	12251	11950	1.245	1.203	1.035	48.8	50.8
19	9550	11805	11866	1.236	1.295	0.955	(47.4)	(45.7)
							47.4	49.3
								(48.8)

one exception, namely, the last measurement for which the linearity correction factor computed by Miller presents an exceedingly high figure. For this reason, this last result seems to be less reliable than the remaining ones, notwithstanding the fact that the specific activity of the sample as obtained by Miller is in good agreement

Table II

A. Set of thick counters of volume difference ΔV = 15.09 cm<sup>3</sup>

V Volts	Long counter		Short counter		Differences	
	cps	cps corr.	cps	cps corr.	cps	cps corr.
1	2		3		4	
2480	37.88	39.68	13.02	13.23	24.86	26.45
2520	38.48	40.34	13.24	13.45	25.24	26.89
2560	39.28	41.22	13.54	13.76	25.74	27.46
2600	39.29	41.23	13.84	14.07	25.45	27.16
2640	39.48	41.44	14.16	14.40	25.32	27.04
2680	40.11	42.14	14.28	14.53	25.83	27.61
2720	40.24	42.28	14.84	15.11	25.40	27.17
					25.41 ± 0.10 cps	
					27.11 ± 0.11 cps	

B. Set of thin counters ΔV = 10.79 cm<sup>3</sup>

2440	28.00	28.97	9.22	9.32	18.78	19.65
2480	28.10	29.08	9.08	9.18	18.02	18.90
2520	28.42	29.42	9.61	9.72	18.81	18.70
2560	28.61	29.63	9.74	9.85	18.87	19.78
2600	29.01	30.06	9.84	9.96	19.17	20.10
2640	29.02	30.07	9.91	10.03	19.11	20.04
					18.76 ± 19.53 ± 0.09 ± 0.08	

with the figures for the remaining results. The average of the first six measurements yields a figure exceeding the result measured by c. a. 4%, thus leading to a  $T_{1/2}$  result by 4% lesser. By Miller's measurements,  $T_{1/2} = 6100$  years. With the correction,  $T_{1/2} = 5864 \pm 200$  years (or  $5925 \pm 250$ , if seven measurements were taken into account).

High precision measurements of  $T_{1/2}^{14}\text{C}$  are due to Hawkings et al., who used sets of two counters differing in length and working in identical conditions. The device eliminated end effects automatically. However, in evaluating the correction for the dead time of the quenching system, the foregoing authors didn't take into consideration the delay between the moment of transition of the ionizing particle and the "discharging" of the counter. The results obtained by them, and the results corrected, are given in *Table II* (detailed results of one measurement) and *Table III* (ultimate results of three measurements).

Table III

Measure- ment	Set of counters	Activity exp. ( $A_1$ )	Activity corr. ( $A_2$ )	$A_2/A_1$
I	Thick	1.684	1.798	1.068
	Thin	1.738	1.842	1.060
II	Thick	0.868	0.890	1.025
	Thin	0.860	0.889	1.034
III	Thick	1.298	1.366	1.052
	Thin	1.257	1.300	1.034
				1.046

It is seen from *Table II* that, when neglecting the effect of delayed pulses, the authors obtained figures for the activity of the samples that were approximately 5% too low. This leads to the corrected value of  $T_{1/2}^{14}\text{C}$  as given by the foregoing authors of  $6320 \pm 200$  to about  $6040 \pm \sim 300$  years. The preliminary character of the  $\Phi(\tau)$ -function can produce a difference in correction-numbers amounting to 10–20%. Nevertheless it seems that the pulse-delay effect in  $\text{CO}_2 + \text{CS}_2$  counters can quantitatively explain the discrepancies in  $T_{1/2}$  measurements.

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# ÉQUATIONS DU POTENTIEL ET DE LA TEMPÉRATURE POUR CONDUCTEURS DANS UN CHAMP MAGNÉTIQUE

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En imposant les conditions stationnaires aux équations de la thermodynamique des phénomènes irréversibles concernant les effets thermo-galvanomagnétiques on obtient les équations du potentiel et de la température. Celles-ci donnent la solution complète du problème pour toutes les conditions aux limites, contrairement au formalisme jusqu'ici en usage. On a prouvé qu'il suffit de donner la valeur de la température à la surface pour obtenir une solution unique dans le cas où le conducteur est en isolation électrique. On a donné une méthode de trouver cette solution. On a montré que dans un tel conducteur peut apparaître un courant électrique stationnaire.

## 1. Introduction

L'article présent est le développement de deux articles publiés dernièrement (Stachowiak 1960).

Avant l'origine de la thermodynamique des phénomènes irréversibles, la théorie des effets thermo- et galvanomagnétiques était basée sur une méthode inexacte dite quasithermodynamique (voir de Groot 1952, Callen 1948).

Callen (1948) a élaboré la théorie de ces effets fondée sur la thermodynamique des phénomènes irréversibles. Les équations phénoménologiques obtenues expriment le courant électrique et le courant d'entropie comme formes linéaires des composantes du gradient du potentiel électrochimique et de la température.

Mazur et Prigogine (1951) ont obtenu des équations un peu différentes, où le gradient du potentiel électrique et le courant de chaleur sont exprimés par le courant électrique et le gradient de température.

Ce problème a été aussi considéré par Fieschi et autres (1954) et de façon relativiste par Kluitenberg et de Groot (1953, 1954, 1955).

Dans l'article présent nous emploierons le formalisme de Callen généralisé sur trois dimensions (voir Landau et Lifshits 1957); celui-ci offre le passage le plus commode aux équations du potentiel et de la température.

Les équations phénoménologiques, dans notre cas au nombre de 6, relient entre elles 12 grandeurs (6 composantes des courants et 6 composantes des gradients) et par conséquent elles ne peuvent donner la résolution complète du problème. Nous devons connaître 6 grandeurs parmi 12 pour fixer les 6 autres. Le but de cet article est d'obtenir les équations du potentiel et de la température qui donnent la résolution complète du problème pour toutes les conditions aux limites. Le formalisme des équations phénoménologiques employé jusqu'ici par les auteurs ne le permettait pas. Nous considérons uniquement les effets linéaires par rapport au champ magnétique. Le conducteur est supposé non ferromagnétique et les coefficients d'Onsager dépendants de la température seule. Le cas d'un conducteur en isolation électrique va nous intéresser particulièrement.

En § 2 nous obtenons les équations du potentiel et de la température et nous examinons les conditions aux limites. En § 3 une méthode de résoudre ces équations est élaborée et la preuve de l'unicité des solutions est donnée. Le § 4 est consacré au problème de l'existence d'un courant électrique stationnaire.

## 2. Les équations du potentiel et de la température

Nous allons nous servir des courants et des affinités employés dans la monographie de de Groot (1952). Alors les équations phénoménologiques à trois dimensions pour un conducteur placé dans un champ magnétique ont l'aspect (comp. Landau et Lifshits 1957)

$$-\vec{J} = l_1 \nabla \mu + l_{12} \nabla T + l_{13} [\nabla \mu, \vec{B}] + l_{14} [\nabla T, \vec{B}], \quad (1a)$$

$$-\vec{S} = l_{12} \nabla \mu + l_2 \nabla T + l_{12} [\nabla \mu, \vec{B}] + l_{24} [\nabla T, \vec{B}], \quad (1b)$$

où  $\vec{J}$  est la densité du courant électrique,  $\vec{S}$  — la densité du courant d'entropie,  $\vec{B}$  — le vecteur de l'induction magnétique;  $l_1, l_2, l_{12}, l_{13}, l_{14}$  et  $l_{24}$  sont les coefficients d'Onsager: particulièrement  $l_1$  est le coefficient de conductibilité électrique,  $l_2 T$  celui de conductibilité thermique;  $\mu$  est le potentiel électrochimique.

$$\mu = \mu_e + \mu_c, \quad (2)$$

où  $\mu_e$  est le potentiel électrique,  $\mu_c$  — le potentiel chimique.

Les équations (1) négligent les effets dépendants des puissances supérieures du champ magnétique. C'est une approximation juste pour les champs magnétiques faibles.

L'application des conditions stationnaires aux équations (1) donne les équations du potentiel et de la température. Ces conditions sont les suivantes (voir Callen 1948):

$$\nabla \cdot \vec{J} = 0, \quad (3a)$$

$$\nabla \cdot \vec{Q} = -\vec{J} \nabla \mu, \quad (3b)$$

où  $\vec{Q}$  est la densité du courant de chaleur

$$\vec{Q} = T \vec{S}. \quad (4)$$

Les équations (1) donnent

$$\begin{aligned} -\nabla \cdot \vec{J} &= l_1 \Delta \mu + l_{12} \Delta T - l_{13} \nabla \mu [\nabla, \vec{B}] - l_{14} \nabla T [\nabla, \vec{B}] + l'_1 \nabla T \nabla \mu + \\ &\quad + l'_{12} (\nabla T)^2 + l'_{13} \vec{B} [\nabla T, \nabla \mu], \\ -\nabla \cdot \vec{Q} &= l_{12} T \Delta \mu + l_2 T \Delta T - l_{14} T \nabla \mu [\nabla, \vec{B}] - l_{24} T \nabla T [\nabla, \vec{B}] + \\ &\quad + (l_{12} T)' \nabla T \nabla \mu + (l_2 T)' (\nabla T)^2 + (l_{14} T)' \vec{B} [\nabla T, \nabla \mu], \end{aligned}$$

où l'apostrophe indique la dérivée par rapport à la température.

Nous pouvons négliger les termes contenant  $\text{rot } \vec{B}$ , car  $\vec{B}$  est de principe un champ extérieur, donc son rotationnel doit être zéro à l'intérieur du conducteur (nous ne nous occupons pas de l'influence que peut avoir le courant électrique présent dans le conducteur sur  $\vec{B}$ ).

Si le courant électrique est proportionnel à  $B$ , ce qui a lieu en effet, comme nous allons voir dans le paragraphe suivant, lorsque le conducteur est isolé au point de vue électrique, on obtient de l'équation (1a)

$$l_1 \nabla \mu + l_{12} \nabla T \sim B.$$

Donc

$$[\nabla \mu, \nabla T] \sim B.$$

Négligeant les termes bilinéaires en  $B$  nous obtenons

$$\begin{aligned} -\nabla \cdot \vec{J} &= l_1 \Delta \mu + l_{12} \Delta T + l'_1 \nabla T \nabla \mu + l'_{12} (\nabla T)^2, \\ -\nabla \cdot \vec{Q} &= l_{12} T \Delta \mu + l_2 T \Delta T + (l_{12} T)' \nabla T \nabla \mu + (l_2 T)' (\nabla T)^2. \end{aligned} \quad (5)$$

Les conditions (3) nous donnent donc les équations suivantes:

$$l_1 \Delta \mu + l_{12} \Delta T + l'_1 \nabla T \nabla \mu + l'_{12} (\nabla T)^2 = 0, \quad (6a)$$

$$l_{12} T \Delta \mu + l_2 T \Delta T + l_1 (\nabla \mu)^2 + [l_{12} + (l_{12} T)'] \nabla T \nabla \mu + (l_2 T)' (\nabla T)^2 = 0. \quad (6b)$$

Les équations (6) ne contiennent pas  $B$ . Donc dans l'approximation que nous suivons les équations du potentiel et de la température ne dépendent pas du champ magnétique, si le conducteur est en isolation électrique. Les conditions aux limites pour un tel conducteur ont la forme

$$T(\sigma) = f(\sigma), \quad (7a)$$

$$J_n = 0, \quad (7b)$$

où  $\sigma$  indique un point de la surface du conducteur et  $J_n$  la composante normale du courant  $\vec{J}$  à la surface. Évidemment les conditions (7) ne sont pas les seules possibles. Nous les choisissons parce qu'elles ont une interprétation physique simple.

Occupons nous de la condition (7b). Choisissons dans un point donné de la surface un système de coordonnées cartésiennes  $n, t, v$ , tel que l'axe  $n$  soit normal à la surface et les axes  $t$  et  $v$  tangents. Alors la condition (7b) prendra la forme

$$l_1 \frac{\partial \mu}{\partial n} + l_{13} B_v \frac{\partial \mu}{\partial t} - l_{13} B_t \frac{\partial \mu}{\partial v} = - \left( l_{12} \frac{\partial T}{\partial n} + l_{14} B_v \frac{\partial T}{\partial t} - l_{14} B_t \frac{\partial T}{\partial v} \right), \quad (8)$$

où autrement

$$\begin{aligned} & [l_1^2 + l_{13}^2 (B_t^2 + B_v^2)]^{1/2} \left( \frac{l_1}{[l_1^2 + l_{13}^2 (B_t^2 + B_v^2)]^{1/2}} \frac{\partial \mu}{\partial n} + \right. \\ & \left. + \frac{l_{13} B_v}{[l_1^2 + l_{13}^2 (B_t^2 + B_v^2)]^{1/2}} \frac{\partial \mu}{\partial t} + \frac{-l_{13} B_t}{[l_1^2 + l_{13}^2 (B_t^2 + B_v^2)]^{1/2}} \frac{\partial \mu}{\partial v} \right) \\ & = - [l_{12}^2 + l_{14}^2 (B_t^2 + B_v^2)]^{1/2} \left( \frac{l_{12}}{[l_{12}^2 + l_{14}^2 (B_t^2 + B_v^2)]^{1/2}} \frac{\partial T}{\partial n} + \right. \\ & \left. + \frac{l_{14} B_v}{[l_{12}^2 + l_{14}^2 (B_t^2 + B_v^2)]^{1/2}} \frac{\partial T}{\partial t} + \frac{-l_{14} B_t}{[l_{12}^2 + l_{14}^2 (B_t^2 + B_v^2)]^{1/2}} \frac{\partial T}{\partial v} \right) \end{aligned} \quad (9)$$

Nous avons donc une égalité entre les dérivées suivant diverses directions. Négligeant les termes carrés en  $B$  nous pouvons écrire

$$\frac{\partial \mu}{\partial s_1} = - \frac{l_{12}}{l_1} \frac{\partial T}{\partial s_2}, \quad (10)$$

où  $\frac{\partial}{\partial s_1}$  et  $\frac{\partial}{\partial s_2}$  indiquent les dérivées suivant les directions définies par

$$\begin{aligned} \vec{s}_1 &= \vec{n} + \frac{l_{13}}{l_1} B_v \vec{t} - \frac{l_{13}}{l_1} B_t \vec{v}, \\ s_2 &= \vec{n} + \frac{l_{14}}{l_{12}} B_v \vec{t} - \frac{l_{14}}{l_{12}} B_t \vec{v}. \end{aligned} \quad (11)$$

$\vec{n}, \vec{t}, \vec{v}$  sont les vecteurs unitaires répondant aux axes  $n, t, v$ .

Nous voyons que le champ magnétique a une influence sur la forme des conditions aux limites. Si  $\vec{B}$  disparaît nous avons un problème de Neumann, en cas contraire nous avons une condition à dérivée oblique, telle que l'angle entre la direction oblique et la direction normale dépend du champ magnétique.



Nous aurions pu imposer des conditions aux limites indépendantes du champ magnétique. Mais dans ce cas le changement du champ magnétique changerait leur sens physique, car  $\vec{B}$  entre dans les équations (1).

### 3. Résolution des équations du potentiel et de la température et problème d'unicité A) en absence du champ magnétique

Avant de nous occuper des équations (6) en présence du champ magnétique, nous devons prouver que la condition sous laquelle elles ont été obtenues, c'est-à-dire que  $\vec{J}$  est proportionnel à  $B$ , est satisfaite.  $\vec{J}(x, y, z)$  est une fonction du champ magnétique. Introduisons une unité d'induction  $\vec{B}_0(x, y, z)$  telle que

$$\vec{B}(x, y, z) = \beta \vec{B}_0(x, y, z), \quad (12)$$

où  $\beta$  est la mesure du champ magnétique.

Si le champ  $\vec{B}$  est faible nous pouvons développer  $\vec{J}$  en série de Taylor:

$$\vec{J} = \vec{J}_0(\vec{r}) + \vec{j}_1(\vec{r}, \vec{B}_0) \beta + \vec{j}_2(\vec{r}, \vec{B}_0) \beta^2 + \dots \quad (13)$$

$\vec{j}_1$  et  $\vec{j}_2$  sont évidemment des fonctions du lieu et des fonctionnelles de  $\vec{B}_0$ . Le premier terme à droite est indépendant du champ magnétique, le second est linéaire en  $B$ , le troisième bilinéaire. Si nous prouvons que  $\vec{J}_0 = 0$ ,  $\vec{J}$  peut être en effet considéré comme proportionnel à  $B$  dans notre approximation.

S'il n'y a pas de champ magnétique, les relations phénoménologiques ont l'aspect

$$-\vec{J} = l_1 \nabla \mu + l_{12} \nabla T, \quad (14)$$

$$-\vec{Q} = l_{12} T \nabla \mu + l_2 T \nabla T. \quad (15)$$

En introduisant (14) et (15) dans (3) nous obtenons les équations (6). Les conditions aux limites auront la forme

$$T(\sigma) = f(\sigma), \quad (16)$$

$$\frac{\partial \mu}{\partial n} = - \frac{l_{12}}{l_1} \frac{\partial T}{\partial n}. \quad (17)$$

Les solutions de ce problème sont des systèmes de fonctions  $\mu(\vec{r})$ ,  $T(\vec{r})$ . Nous allons démontrer qu'une fonction  $T(\vec{r})$  donnée ne peut entrer que dans un seul système  $\mu(\vec{r})$ ,  $T(\vec{r})$  constituant une solution, c'est-à-dire que si nous connaissons  $T(\vec{r})$  qui est l'une des fonctions dont se compose la solution, la seconde fonction  $\mu(\vec{r})$  est unique, à part une constante additive. En effet, si  $T(\vec{r})$  est une fonction donnée, l'équation (6a) est du type

$$\Delta \mu + \sum_{i=1}^3 f_i(\vec{r}) \frac{\partial \mu}{\partial x_i} = g(\vec{r}) \quad (18)$$

avec la condition aux limites

$$\frac{\partial \mu}{\partial n} = h(\sigma). \quad (19)$$

Ce problème n'a qu'une seule solution, mettant à part une constante additive (voir Miranda 1955).

Il est facile de voir que  $\mu$  remplissant la relation

$$\nabla \mu = -\frac{l_{12}}{l_1} \nabla T \quad (20)$$

est une solution particulière de (6a). Puisque  $l_{12}$ ,  $l_1$  dépendent uniquement de la température, la part droite de (20) peut être écrite sous la forme d'un gradient. La relation (20) définit  $\mu$  univoquement, à part une constante additive,  $\mu$  satisfaisant à (20) satisfait aussi la condition (17) et constitue par conséquent la seule solution du problème (la constante additive n'a pas d'influence sur la relation (20)). En introduisant (20) dans (14) et (15) nous constatons que  $\vec{J} = 0$ , et

$$-\vec{Q} = C(T) \nabla T, \quad (21)$$

où

$$C(T) = \frac{(l_1 l_2 - l_{12}^2) T}{l_1}. \quad (22)$$

Introduisant (21) dans (3b) nous obtenons

$$\nabla \cdot (C(T) \nabla T) = 0 \quad (23)$$

avec la condition aux limites (16). Ce problème n'a qu'une seule solution, car nous pouvons passer de la variable  $T$  à la variable  $\Theta$  définie par l'intégrale (voir Carslaw, Jaeger 1959)

$$\Theta(\vec{r}) = \frac{1}{C(\tau)} \int_{\tau}^{\vec{T}(\vec{r})} C(T) dT, \quad (24)$$

où  $\tau$  a une valeur quelconque mais fixée. Introduisant (24) dans (23) nous obtenons l'équation de Laplace

$$\Delta \Theta = 0 \quad (25)$$

avec la condition aux limites

$$\Theta(\sigma) = \frac{1}{C(\tau)} \int_{\tau}^{f(\sigma)} C(T) dT. \quad (26)$$

Ce problème bien sûr a une solution unique. Le passage de  $\Theta$  à  $T$  est univoque, si le coefficient  $C(T)$  a toujours le même signe. Le deuxième principe de la thermodyna-

mique appliqué à (21) fait que cette condition est remplie (la direction du courant de chaleur est inverse à celle du gradient de température).

Nous voyons donc

1) que le problème (6), (7) en absence du champ magnétique n'a qu'une seule solution.

2) qu'il n'y a pas de courant électrique.

### *B) en présence du champ magnétique.*

Nous avons le système d'équations (6) et les conditions aux limites (7a) et (10). La relation (20) satisfait toujours à l'équation (6a), mais elle ne remplit plus la condition aux limites, car  $\vec{s}_1$  et  $\vec{s}_2$  dans (10) n'indiquent pas la même direction. Nous divisons  $\mu$  en deux parties selon la formule

$$\nabla \mu = -\frac{l_{12}}{l_1} \nabla T + \nabla \varphi. \quad (27)$$

Introduisant (27) dans les équations (6) nous obtenons

$$l_1 \Delta \varphi + l_1' \nabla T \nabla \varphi = 0, \quad (28)$$

$$\nabla \cdot (C(T) \nabla T) + \nabla \cdot (l_{12} T \nabla \varphi) - l_{12} \nabla T \nabla \varphi + l_1 (\nabla \varphi)^2 = 0 \quad (29)$$

avec les conditions aux limites

$$T(\sigma) = f(\sigma), \quad (7a)$$

$$\frac{\partial \varphi}{\partial n} = \frac{L}{l_1} \left( B_v \frac{\partial f}{\partial t} - B_t \frac{\partial f}{\partial v} \right), \quad (30)$$

où

$$L = \frac{l_{12} l_{13} - l_1 l_{14}}{l_1}. \quad (31)$$

Apercevons que la part droite des conditions aux limites ne contient maintenant que des fonctions connues.

Nous passons à la variable  $\Theta$  à l'aide de la transformation (24), ce qui permet d'écrire

$$l_1 \Delta \varphi + l_1 \nabla \Theta \nabla \varphi = 0, \quad (32)$$

$$C(\tau) \Delta \Theta = -l_1 \frac{d}{d\Theta} \left( \frac{l_{12}}{l_1} \right) T(\Theta(r)) \nabla \Theta \nabla \varphi \quad (33)$$

avec les conditions aux limites (26) et (30). Le point indique la dérivée par rapport à  $\Theta$ .

La relation (27) prend la forme

$$\nabla \mu = -\frac{l_{12}}{l_1} \frac{C(\tau)}{C(\Theta)} \nabla \Theta + \nabla \varphi. \quad (34)$$

$\Theta(\vec{r})$  et  $\varphi(\vec{r})$  peuvent être développés en série de Taylor selon  $B$ , ainsi que  $\vec{J}$  (voir (13)):

$$\Theta(\vec{r}) = \Theta_0(\vec{r}) + \beta \vartheta_1(\vec{r}), \quad (35)$$

$$\varphi(\vec{r}) = \beta \varphi_1(\vec{r}). \quad (36)$$

Les termes non linéaires en  $B$  ont été négligés. Introduisant (35) et (36) dans (32) et (33) nous obtenons dans l'approximation linéaire en  $B$

$$\Delta \Theta_0 = 0, \quad (37)$$

$$l_1 \Delta \varphi + l_1 \nabla \Theta_0 \nabla \varphi = 0, \quad (38)$$

$$C(\tau) \Delta \Theta_1 = -l_1 \frac{d}{d\Theta_0} \left( \frac{l_{12}}{l_1} \right) T(\Theta_0) \nabla \Theta_0 \nabla \varphi, \quad (39)$$

où  $\Theta_1$  est défini selon la formule

$$\Theta = \Theta_0 + \Theta_1. \quad (40)$$

Les conditions aux limites sont les suivantes:

$$\Theta_0(\sigma) = \frac{1}{C(\tau)} \int_{\tau}^{f(\sigma)} C(T) dT, \quad (41)$$

$$\frac{\partial \varphi}{\partial n} = \frac{L}{l_1} \left( B_v \frac{\partial f}{\partial t} - B_t \frac{\partial f}{\partial v} \right), \quad (42)$$

$$\Theta_1(\sigma) = 0. \quad (43)$$

Nous résolvons d'abord l'équation (37) sous la condition (41). Ce problème n'a qu'une seule solution. Puis nous introduisons  $\Theta_0$  ainsi obtenu dans l'équation (38) et nous cherchons la solution de cette dernière sous la condition (42). Diverses solutions d'un tel problème ne peuvent différer que d'une constante additive (voir Miranda 1955). Ensuite nous introduisons  $\varphi$  et  $\Theta_0$  dans l'équation (39). (39) et (43) donnent une solution unique, la constante additive dans  $\varphi$  ne joue évidemment aucun rôle.

#### 4. Le rotationnel du courant électrique

Puisque la divergence de  $\vec{J}$  disparaît et qu'il n'y a pas d'afflux de l'extérieur, s'il y a un courant électrique, il doit y avoir des lieux où  $\text{rot } \vec{J} \neq 0$  (à moins que le conducteur ne soit pas simplement connexe) et réciproquement, si  $\text{rot } \vec{J}$  n'est pas zéro dans tout le conducteur, il doit y avoir un courant électrique. Calculons donc  $\text{rot } \vec{J}$  à partir de l'équation (1a), en nous servant de (27):

$$\begin{aligned} -[\nabla, \vec{J}] &= l'_1 [\nabla T, \nabla \varphi] - L' [\nabla T, [\nabla T, \vec{B}]] + \\ &+ L \vec{B} \Delta T - L (\vec{B} \nabla) \nabla T + L (\nabla T \nabla) \vec{B}. \end{aligned} \quad (44)$$

Si nous négligeons la dépendance thermique des coefficients et appliquons un champ

magnétique homogène

$$[\nabla, \vec{J}]_{\xi} = -LB \left( \frac{\partial^2 T}{\partial \xi^2} + \frac{\partial^2 T}{\partial \eta^2} \right), \quad (45)$$

où  $\xi, \eta, \zeta$  sont des coordonnées cartésiennes telles que l'axe  $\zeta$  est parallèle à  $\vec{B}$ . Nous voyons que, si les secondes dérivées de la température ne disparaissent pas, même dans un conducteur isolé au point de vue électrique peu apparaît un courant électrique stationnaire.

### Conclusions

L'application des conditions stationnaires aux relations phénoménologiques concernant les effets thermo-galvanomagnétiques mène aux équations du potentiel et de la température. Ces équations, dans l'approximation linéaire ne contiennent pas le vecteur de l'induction magnétique. Le champ magnétique a par contre une influence sur la forme des conditions aux limites. Parmi les conditions possibles nous choisissons celles qui correspondent à l'isolement électrique du conducteur, avec une répartition fixée de la température à la surface.

Nous avons obtenu une méthode de résolution de ce problème dans l'approximation linéaire en  $B$ . Nous avons démontré que dans cette approximation le problème a une solution unique, mettant à part une constante additive dans le potentiel. Les approximations supérieures de la solution seraient dépourvues de sens, car les relations originelles ne sont exactes que dans l'approximation linéaire.

Le calcul du rotationnel du courant électrique montre que même dans notre cas d'isolement électrique, un courant électrique peut exister, si les secondes dérivées de la température ne sont pas zéro.

La résolution des équations du potentiel et de la température et un examen plus minutieux des conditions d'existence d'un courant électrique stationnaire dans les cas les plus simples auront lieu dans un article prochain.

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PROTON SPIN-LATTICE RELAXATION TIMES IN VERY DILUTE AQUEOUS SOLUTIONS OF  $\text{Ni}^{++}$  AND  $\text{Mn}^{++}$  IONS

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Proton magnetic spin-lattice relaxation time  $T_1$  in air-free aqueous solutions in the  $\text{Ni}^{++}$  concentration range between  $2 \times 10^{16}$  and  $2 \times 10^{18}$  ions/cm<sup>3</sup> was measured. For  $\text{Ni}^{++}$  and  $\text{Mn}^{++}$  ions the dependence of  $1/T_1$  on concentration throughout the temperature range 10 — 90°C was shown to be linear. A simple method was developed for obtaining air-free samples of aqueous solutions.

## 1. Introduction

The addition of paramagnetic ions to water decreases the proton spin-lattice and spin-spin relaxation times,  $T_1$  and  $T_2$ . This effect was first interpreted by Bloembergen et al. (1948) in terms of an ion-proton magnetic dipol-dipol interaction, which predicted a proportional dependence of  $1/T_1$  on the concentration:

$$1/T_1 = kc, \quad (1)$$

where  $c$  is the concentration and  $k$  is a function of the temperature only. This dependence is found to be correct for not too weak solutions.

In the case of very dilute solutions the interaction between protons must also be taken into account. As  $1/T_1$  is proportional to the transition probability and because of the additivity of transition probabilities resulting from the two interactions, the expression for  $1/T_1$  is of the following form:

$$1/T_1 = 1/T_{1w} + kc. \quad (2)$$

$T_{1w}$  represents the proton spin-lattice relaxation time in pure water.

Recently new theories of nuclear relaxation processes in paramagnetic ions solutions were developed (Bloembergen 1957, Hausser and Laukien 1959, Bernheim et al. 1959). These theories, successful in explaining the inequality of  $T_1$  and  $T_2$  in

some ion solutions, also take into account scalar coupling between the nuclear spin of the proton and the electron spin of the paramagnetic ion. With respect to these theories, eqs. (1) and (2) still remain valid.

In the range of medium and strong concentrations of paramagnetic ions,  $T_1$  measurements were made by a number of authors. The most extensive investigations of the concentration dependence of  $T_1$  (and  $T_2$ ) were carried out by Laukien and Schlüter (1956), Nolle and Morgan (1957) and Laukien and Noack (1958). The results obtained prove the validity of eq. (1).

In the low concentration range, where  $T_1 > 0.1 T_{1w}$ , only few results for air-free solutions are known. Giulotto (1956) carried out measurements of  $T_1$  in water and some organic liquids containing the paramagnetic gases  $O_2$  and  $NO$  in solution. His results corroborate the validity of eq. (2) in this case.

In the present paper measurements of  $T_1$  in the above mentioned low concentration range of paramagnetic ions  $Ni^{++}$  and  $Mn^{++}$  are presented. These ions were chosen because of their different  $T_1/T_2$  ratio behaviour and absence of hydrolysis effects.

## 2. Preparation of Samples

As the atmospheric oxygen dissolved in water affects  $T_1$  considerably, it was necessary to develop a method for preparing air-free solutions. This was achieved by boiling at length in the simple glass apparatus shown in Fig. 1.

A known amount of paramagnetic salt in aqueous solution was introduced into the glass bulb (a), which was then filled up with carefully purified water. The inlet tube was sealed off at point (b). By heating the bulb, the solution was evaporated to

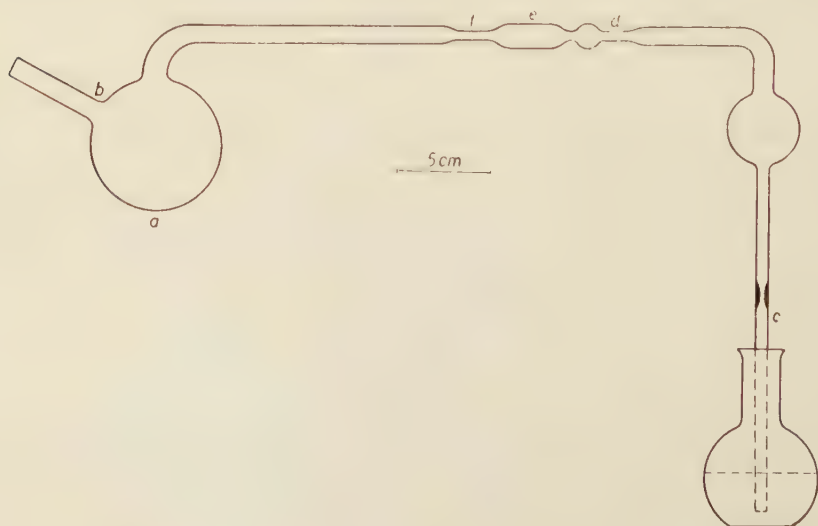


Fig. 1. Glass apparatus for preparing air-free solutions.

approximately 1/4 of its initial volume. The steam carrying away the air in solution escaped through tube (c), the end of which was immersed in water. On switching off the heater, the water level in tube (c) began to rise and at this moment the apparatus was sealed off at (d) yielding a closed system containing the air-free solution.

The arrangement together with the sealed off tubings was weighed to determine the concentration of the solution. Subsequently the solution was poured into the small bulb (e) constituting the future sample, which was then sealed off at (f).

For preparing the solutions, A.R. grade  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  were used. Water was purified by the following method: ordinary laboratory distilled water was treated with  $25 \times 10^{-3}$  g  $\text{KMnO}_4$ , 1 g  $\text{AlK}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  and 0.7 g  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  per litre and then distilled twice:

High purity of the glass apparatus used was most essential.

### 3. Experimental Procedure for $T_1$ Measurements

A method described elsewhere (Hennel and Hryniewicz, 1958) was used for  $T_1$  measurements at 28 Mc/sec.

For detecting the nuclear magnetic resonance, the high frequency bridge described by Grivet et al. (1951) was used. The bridge was mounted in a box made of a brass block. The entire bridge device containing the sample was kept at the constant temperature required. This was carried out by letting water flow from a thermostat through copper tubings soldered within the block.

The temperature was measured with a glass-mercury thermometer mounted in the outlet tube of the block. The readings of this thermometer were calibrated by comparison with an exact resistance thermometer situated in place of the sample. The corrections obtained amounted to  $(0 \pm 0.1)^\circ\text{C}$  for  $20^\circ\text{C}$  and  $(1.5 \pm 0.3)^\circ\text{C}$  for  $90^\circ\text{C}$ , and were reproducible.

### 4. Results and Discussion

The resulting values of  $T_1$  for  $20^\circ\text{C}$  are shown in Fig. 2 versus the  $\text{Ni}^{++}$  ions concentration. The theoretical curve drawn according to eq. (2) assuming<sup>1</sup>  $T_{1w} = 3.1$  sec and  $k = 1.02 \times 10^{-18}$  cm<sup>3</sup>/ion. sec is also shown. This value of  $k$  at  $20^\circ\text{C}$  was calculated from the data obtained for the much greater  $\text{Ni}^{++}$  concentration of  $5.5 \times 10^{20}$  ions/cm<sup>3</sup> by Hausser and Laukien (1958) at 26.5 Mc/sec.

All  $T_1$  measurements in the present investigation were accurate to 3%.

The experimental results in Fig. 2 support eq. (2) and show that  $k$  remains constant throughout the concentration range of  $2.38 \times 10^{16}$  to  $5.5 \times 10^{20}$  ions/cm<sup>3</sup>. This can be stated to an accuracy of about 10%, except for the lowest concentration range of about  $3 \times 10^{16}$  ions/cm<sup>3</sup>, where the accuracy is 30%. Taking into account the measurements of Laukien and Schlüter (1956), the constancy of  $k$  at room temper-

1) The interpolated value of  $T_1$  for water at  $20^\circ\text{C}$  is from Hennel et al. 1958. Other values are 3.1 sec (Giulotto et al. 1957), and 2.92 sec (Simpson and Carr 1958).

ature throughout the  $\text{Ni}^{++}$  concentration range of  $2.38 \times 10^{16}$  to  $2.3 \times 10^{20}$  ions/cm<sup>3</sup> has been proved.

To investigate the validity of eq. (2) in the case of  $\text{Mn}^{++}$  ions, two samples containing  $1.19 \times 10^{16}$  and  $1.33 \times 10^{16}$   $\text{Mn}^{++}$  ions/cm<sup>3</sup> were prepared. The measured  $T_1$  values at 20°C were 1.97 sec and 1.92 sec respectively, and the calculated  $k$  values —

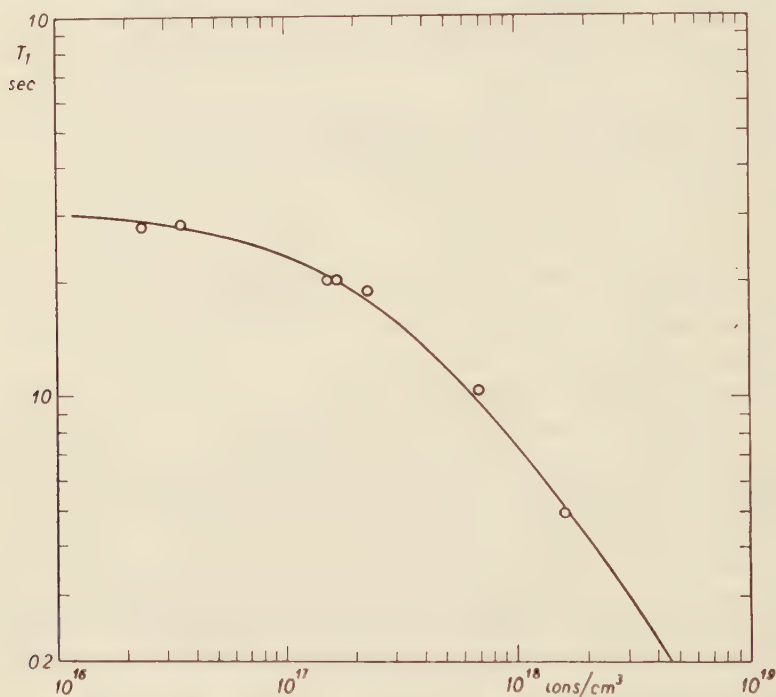


Fig. 2. Proton relaxation time  $T_1$  versus the concentration of  $\text{Ni}^{++}$  ions in oxygen-free water at 20°C  
o experimental, — theoretical.

$1.55 \times 10^{-17}$  and  $1.49 \times 10^{-17}$  cm<sup>3</sup> per ion and sec. This is in good agreement with the value  $k = 1.46 \times 10^{-17}$  obtained at the much higher concentration of  $3 \times 10^{18}$  ions/cm<sup>3</sup> by Bernheim et al. (1959, Fig. 1) at the same frequency and temperature.

To investigate the validity of eq. (2) in the temperature range between 10°C and 90°C, three of the afore mentioned samples (two containing  $\text{Ni}^{++}$  ions and one containing  $\text{Mn}^{++}$  ions) were used for  $T_1$  measurements at different temperatures. The results are compared with  $T_1$  values found at much higher concentrations by calculating the expression:

$$c_{\text{calc}} = (1/T_1 - 1/T_{1h}) T_{1h} \cdot c_h$$

where  $T_{1h}$  is the spin-lattice relaxation time at high concentration  $c_h$ . This expression, according to eq. (2), should be independent of the temperature and  $c_{\text{calc}}$  equal to the concentration of the sample. This is shown in Table I and proves the validity of eq. (2) throughout the temperature range 10–90°C. To obtain  $c_{\text{calc}}$  we used  $T_1$



values interpolated from our experimental results shown in Fig. 3. The  $T_{1h}$  values are taken from Hausser and Laukien (1959) at  $c_h = 5.5 \times 10^{20}$  Ni<sup>++</sup> ion/cm<sup>3</sup> and from Bernheim et al. (1959) at  $c_h = 3 \times 10^{18}$  Mn<sup>++</sup> ions/cm<sup>3</sup>.

Fig. 3 shows the temperature dependence of the function  $A = T_1 \eta / T$  (wherein  $\eta$  is the viscosity of water, and  $T$  — the absolute temperature) as found experimentally

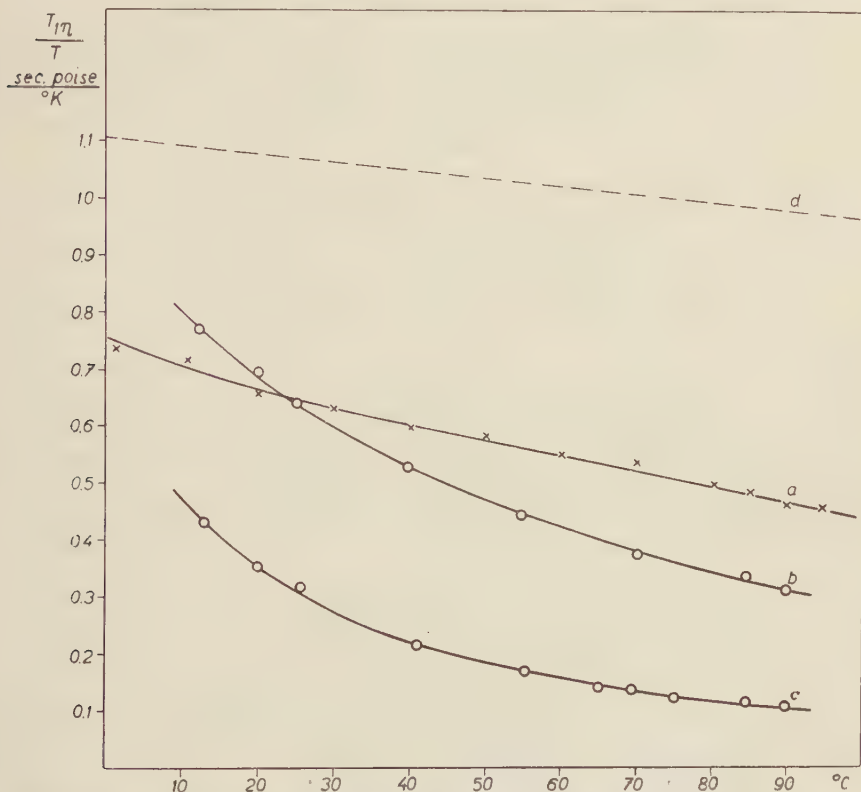


Fig. 3. Temperature dependence of the function  $T_1 \eta / T$  for very dilute aqueous solutions of paramagnetic ions:

(a)  $1.33 \times 10^{16}$  Mn<sup>++</sup> ions/cm<sup>3</sup>, (b)  $1.53 \times 10^{17}$  Ni<sup>++</sup> ions/cm<sup>3</sup>, (c)  $6.89 \times 10^{17}$  Ni<sup>++</sup> ions/cm<sup>3</sup>, and (d) pure water (Hennel et al. 1958), for comparison.

for the three solutions of paramagnetic ions. This function should be constant according to Bloembergen et al. (1948), but, as a matter of fact, it decreases towards higher temperatures even in pure water (Giulotto 1957, Hennel et al. 1958, Simpson and Carr 1958). It is seen from Fig. 3 that a small amount of paramagnetic ions causes a considerable rise in the slope of the  $A$  curve. This can be explained by the temperature dependence of  $k$  for the ion under consideration.

The foregoing fact can have some influence on the unexplained behaviour of  $A$  in pure water, as even in very carefully purified water the presence of some slight paramagnetic contamination is possible.

Table I.

Concentration  $c_{\text{calc}} = (1/T_1 - 1/T_{1w}) T_{1h} \cdot c_h$  as calculated from  $T_1$  at various temperatures ( $^{\circ}\text{C}$ ). Interpolated values of  $T_{1w}$  are given in Table II. The concentration is in  $10^{18}$  ions/ $\text{cm}^3$  units.

Ion	Experimental concentration	Calculated concentration $c_{\text{calc}}$								$c_h$
		10°	15°	20°	40°	50°	60°	80°	90°	
Ni <sup>++</sup>	15.3	17.1	17.1	17.0±3	16.9	16.9	16.2	16.4±1.5	16.6	55000
Ni <sup>++</sup>	68.9	62.0	62.7	63.5±6	64.6	64.6	64.7	65.0±4	63.8	55000
Mn <sup>++</sup>	1.33	1.36	1.38	1.40±0.3	1.46	1.42	1.43	1.44±0.2	1.48	300

Table II.

Interpolated values of the spin-lattice relaxation time  $T_{1w}$  for oxygen-free water at various temperatures (Hennel et al. 1958).

$^{\circ}\text{C}$	0	10	15	20	30	40	50	60	80	90
$T_{1w}$ (sec)	1.72	2.35	2.7	3.1	4.0	5.0	6.05	7.2	9.8	11.3

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# SUPPLEMENTARY NOTE TO THE PAPER: MOLECULAR THEORY OF LIGHT SCATTERING BY MULTI- -COMPONENT SYSTEMS

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The present note is to supplement the paper on a "Molecular Theory of Light Scattering by Multi-Component Systems" (Kielich, 1960), and brings a discussion of the scattered light intensity for the case of a system whose various components consist of quadrupolar, anisotropically polarizable and hyperpolarizable molecules.

The light intensity scattered at the angle  $\vartheta$  is given by the general formula (see, Kielich, 1960)

$$I(\vartheta) = \frac{8\pi^4 I_0}{45 \lambda^4 R_0^2} \{5(1 + \cos^2 \vartheta) F_{\text{is}}(s) + (13 + \cos^2 \vartheta) F_{\text{anis}}(s)\} \quad (1)$$

where  $I_0$  and  $\lambda$  denote the intensity and wave-length of the incident light, respectively and  $R_0$  is the distance of the point of observation from the centre of the scattering volume  $V$ . The factors  $F_{\text{is}}(s)$  and  $F_{\text{anis}}(s)$  characterize the molecular mechanism of isotropic and anisotropic light scattering, respectively. For a multi-component system these are of the form

$$F_{\text{is}}(s) = \sum_{i,j} \left\langle \delta_{\alpha\beta} \delta_{\gamma\delta} \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \frac{\partial m_{\alpha}^{(p,i)}}{\partial E_{\beta}^{(p,i)}} \left( \frac{\partial m_{\gamma}^{(q,j)}}{\partial E_{\delta}^{(q,j)}} \right)^* e^{-is \cdot \mathbf{r}_{ij}^{(pq)}} \right\rangle, \quad (2)$$

$$F_{\text{anis}}(s) = \frac{1}{2} \sum_{i,j} \left\langle (3\delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\beta} \delta_{\gamma\delta}) \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \frac{\partial m_{\alpha}^{(p,i)}}{\partial E_{\beta}^{(p,i)}} \left( \frac{\partial m_{\gamma}^{(q,j)}}{\partial E_{\delta}^{(q,j)}} \right)^* e^{-is \cdot \mathbf{r}_{ij}^{(pq)}} \right\rangle, \quad (3)$$

where  $x_i$  is the mole fraction of the  $i$ -th component,  $m_{\alpha}^{(p,i)}$  — the  $\alpha$ -component of the electric dipole moment induced by the electric field  $E_{\alpha}$  of the incident light wave in the  $p$ -th molecule of species  $i$ ,  $\mathbf{r}_{ij}^{(pq)}$  — the vector connecting the centres of the

$p$ -th and  $q$ -th molecules of the  $i$ -th and  $j$ -th species, and, for Rayleigh scattering,  $|\mathbf{s}| = (4\pi/\lambda) \sin(\theta/2)$ . The brackets  $\langle \rangle$  in eqs. (2) and (3) denote the statistical average in the absence of the external electric field ( $\mathbf{E} = 0$ ) and  $\delta_{\alpha\beta}$  is the substitution tensor (unity if  $\alpha = \beta$  and zero when  $\alpha \neq \beta$ ).

The total differential polarizability tensor of the molecule immersed in the medium is given by the following expansion (for  $\mathbf{E} = 0$ ):

$$\left( \frac{\partial m_{\alpha}^{(p,i)}}{\partial E_{\chi}^{(p,i)}} \right)_{E=0} = \left\{ \alpha_{\alpha\beta}^{(p,i)} + \beta_{\alpha\beta\gamma}^{(p,i)} F_{\gamma}^{(p,i)} + \frac{1}{2} \gamma_{\alpha\beta\gamma\delta}^{(p,i)} F_{\gamma}^{(p,i)} F_{\delta}^{(p,i)} + \dots + \frac{1}{3} B_{\alpha\beta:\gamma\delta}^{(p,i)} F_{\gamma\delta}^{(p,i)} + \dots \right\} \left\{ \delta_{\beta\chi} + \frac{\partial F_{\beta}^{(p,i)}}{\partial E_{\chi}^{(p,i)}} \right\}_{E=0}, \quad (4)$$

with  $\alpha_{\alpha\beta}^{(p,i)}$  denoting the polarizability tensor of the  $p$ -th molecule of species  $i$ , and  $\beta_{\alpha\beta\gamma}^{(p,i)}$ ,  $\gamma_{\alpha\beta\gamma\delta}^{(p,i)}$  —its hyperpolarizability tensors. The tensor  $B_{\alpha\beta:\gamma\delta}^{(p,i)}$  accounts for the additional polarization of the  $p$ -th molecule of species  $i$  as induced by the field gradient  $F_{\alpha\beta}^{(p,i)}$ . The tensors  $\alpha_{\alpha\beta}$ ,  $\beta_{\alpha\beta\gamma}$ ,  $\gamma_{\alpha\beta\gamma\delta}$  and  $B_{\alpha\beta:\gamma\delta}$  have been discussed by Buckingham (1959).  $F_{\alpha}^{(p,i)}$  and  $F_{\alpha\beta}^{(p,i)}$  are the  $\alpha$ -component of the molecular field and  $\alpha\beta$ -component of the field gradient at the centre of molecule  $p$  of species  $i$  due to the electric charge distributions of all the others, in the presence of the electric field  $E_{\alpha}$ .

Substituting the expansion of eq. (4) in eqs. (2) and (3), the following expressions are obtained:

$$F_{is}(s) = \sum_{i,j} \langle \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \{ \alpha_{\alpha\alpha}^{(i)} \alpha_{\beta\beta}^{(j)} + A_{\alpha\alpha:\beta\beta}^{(ij)} + H_{\alpha\alpha:\beta\beta}^{(ij)} \} \cos \mathbf{s} \cdot \mathbf{r}_{ij}^{(pq)} \rangle \quad (5)$$

$$F_{anis}(s) = \frac{1}{2} \sum_{i,j} \langle \sum_{p=1}^{x_i N} \sum_{q=1}^{x_j N} \{ \alpha_{\alpha\beta}^{(i)} \alpha_{\gamma\delta}^{(j)} + A_{\alpha\beta:\gamma\delta}^{(ij)} + H_{\alpha\beta:\gamma\delta}^{(ij)} \} \{ 3\omega_{\alpha\gamma}^{(pq;ij)} \omega_{\beta\delta}^{(pq;ij)} - \delta_{\alpha\beta} \delta_{\gamma\delta} \} \cos \mathbf{s} \cdot \mathbf{r}_{ij}^{(pq)} \rangle. \quad (6)$$

Here,  $\omega_{\alpha\gamma}^{(pq;ij)}$  denotes the cosine of the angle subtended by the  $\alpha$  and  $\gamma$  axes of the molecular systems of reference rigidly attached to the  $p$ -th and  $q$ -th molecules of species  $i$  and  $j$  respectively. The tensors

$$A_{\alpha\beta:\gamma\delta}^{(ij)} = \alpha_{\alpha\beta}^{(i)} \alpha_{\gamma\delta}^{(j)} \frac{\partial F_{\epsilon}^{(j)}}{\partial E_{\delta}^{(j)}} + \alpha_{\gamma\delta}^{(j)} \alpha_{\alpha\beta}^{(i)} \frac{\partial F_{\epsilon}^{(i)}}{\partial E_{\beta}^{(i)}} + \alpha_{\alpha\epsilon}^{(i)} \alpha_{\gamma\eta}^{(j)} \frac{\partial F_{\epsilon}^{(i)}}{\partial E_{\beta}^{(i)}} \frac{\partial F_{\eta}^{(j)}}{\partial E_{\delta}^{(j)}}, \quad (7)$$

$$H_{\alpha\beta:\gamma\delta}^{(ij)} = \alpha_{\alpha\beta}^{(i)} \beta_{\gamma\delta\epsilon}^{(j)} F_{\epsilon}^{(j)} + \alpha_{\gamma\delta}^{(j)} \beta_{\alpha\beta\epsilon}^{(i)} F_{\epsilon}^{(i)} + \dots + \frac{1}{2} \alpha_{\alpha\beta}^{(i)} \gamma_{\gamma\delta\epsilon\eta}^{(j)} F_{\epsilon}^{(i)} F_{\eta}^{(j)} + \frac{1}{2} \alpha_{\gamma\delta}^{(j)} \gamma_{\alpha\beta\epsilon\eta}^{(i)} F_{\epsilon}^{(j)} F_{\eta}^{(i)} + \dots + \frac{1}{3} \alpha_{\alpha\beta}^{(i)} B_{\gamma\delta:\epsilon\eta}^{(j)} F_{\epsilon\eta}^{(j)} + \frac{1}{3} \alpha_{\gamma\delta}^{(j)} B_{\alpha\beta:\epsilon\eta}^{(i)} F_{\epsilon\eta}^{(i)} + \dots \quad (8)$$

determine the effect of the anisotropy of the molecular field and that of the hyperpolarizability of the molecules on light scattering in a dense medium.

With respect to Onsager's (1936) model, the anisotropy of the molecular field is given by

$$\frac{\partial F_{\alpha}^{(i)}}{\partial E_{\beta}^{(i)}} = \psi_{\alpha}^{(i)} \delta_{\alpha\beta} \quad (9)$$

and the molecular field  $F_{\alpha}^{(i)}$  and field gradient  $F_{\alpha\beta}^{(i)}$  at  $\mathbf{E} = 0$  are

$$F_{\alpha}^{(i)} = \chi_{\alpha}^{(i)} \frac{\mu_{\alpha}^{(i)}}{\alpha_{(i)}} + \xi_{\alpha}^{(i)} \frac{\Theta_{\alpha\beta}^{(i)} r_{\beta}}{\alpha_{(i)}^{3/2}}, \quad (10)$$

$$F_{\alpha\beta}^{(i)} = \frac{\partial F_{\alpha}^{(i)}}{\partial r_{\beta}} = \xi_{\alpha}^{(i)} \frac{\Theta_{\alpha\beta}^{(i)}}{\alpha_{(i)}^{3/2}}, \quad (11)$$

wherein  $\mu_{\alpha}^{(i)}$  is the  $\alpha$ -component of the permanent electric dipole moment of an isolated polar molecule of species  $i$  and  $\Theta_{\alpha\beta}^{(i)}$ —its electric quadrupole moment. The parameters  $\psi_{\alpha}^{(i)}$ ,  $\chi_{\alpha}^{(i)}$  and  $\xi_{\alpha}^{(i)}$  are given by:

$$\psi_{\alpha}^{(i)} = \frac{2(n^2 - 1) \{ (n^2 + 2) (n_i^2 - 1) \lambda_{\alpha}^{(i)} - (n_i^2 + 2) (n^2 - 1) \}}{(n^2 + 2) \{ (2n^2 + 1) (n_i^2 + 2) - 2 (n^2 - 1) (n_i^2 - 1) \lambda_{\alpha}^{(i)} \}}, \quad (12)$$

$$\chi_{\alpha}^{(i)} = \frac{2(\varepsilon - 1) (n_i^2 - 1)}{(2\varepsilon + 1) (n_i^2 + 2) - 2(\varepsilon - 1) (n_i^2 - 1) \lambda_{\alpha}^{(i)}}, \quad (13)$$

$$\xi_{\alpha}^{(i)} = 3 \left( \frac{2\varepsilon + 1}{3\varepsilon + 2} \right) \left( \frac{n_i^2 - 1}{n_i^2 + 2} \right)^{3/2} \chi_{\alpha}^{(i)}, \quad (14)$$

where  $\varepsilon$  and  $n$  are the electric permittivity and refractive index of the medium, respectively, and  $\lambda_{\alpha}^{(i)} = \alpha_{\alpha}^{(i)} / \alpha_{(i)}$ , with  $\alpha_{\alpha}^{(i)}$  denoting the polarizability component in the direction of an  $\alpha$ -principal axis of an isolated molecule of species  $i$ , and  $\alpha_{(i)}$ —its mean polarizability.

For non-dipolar molecules ( $\mu_{\alpha} = \beta_{\alpha\beta\gamma} = 0$ ) possessing the axial symmetry, the following tensor elements only are non-vanishing:  $\alpha_{\alpha\beta}$ ,  $\Theta_{\alpha\beta}$ ,  $\gamma_{\alpha\beta\gamma\delta}$  and  $B_{\alpha\beta;\gamma\delta}$  (the axis of symmetry being parallel to 03, see Buckingham 1959):

$$\begin{aligned} \alpha_{11} = \alpha_{22} = \alpha_{\perp}, \quad \gamma_{1111} = \gamma_{2222} = 3\gamma_{1122} = \gamma_{\perp}, \quad \gamma_{1133} = \gamma_{2233} = \gamma_{\parallel}, \\ \alpha_{33} = \alpha_{\parallel}, \quad \gamma_{3333} = \gamma_{\parallel}, \quad \Theta_{33} = -2\Theta_{11} = -2\Theta_{22} = \Theta, \\ B_{33;33} = -2B_{33;11} = -2B_{33;22} = 2(B_{11;11} + B_{11;22}) = B, \end{aligned} \quad (15)$$

where  $\Theta$  is the quadrupole moment of the axially symmetric molecule and  $B$ —its quadrupole polarizability.

With respect to (15) and for  $\lambda \gg r_{ij}$ , the molecular factors of isotropic and anisotropic light scattering assume the form:

$$\begin{aligned} F_{\text{is}} = 9N \sum_{i,j} \alpha_{(i)} \alpha_{(j)} \{ 1 + A_{\text{is}}^{(ij)} + H_{\text{is}}^{(ij)} \} \times \\ \times \left\{ x_i \delta_{ij} + x_i x_j \int \left[ g_{ij}(\tau) - \frac{N}{V} \right] d\bar{\tau} \right\}, \end{aligned} \quad (16)$$

$$\begin{aligned} F_{\text{anis}} = 9N \sum_{i,j} \alpha_{(i)} \delta_{\alpha(i)} \alpha_{(j)} \delta_{\alpha(j)} \{ 1 + A_{\text{anis}}^{(ij)} + H_{\text{anis}}^{(ij)} \} \times \\ \times \left\{ x_i \delta_{ij} + \frac{1}{2} x_i x_j \int (3\cos^2 \Theta_{ij} - 1) \left[ g_{ij}(\tau) - \frac{N}{V} \right] d\bar{\tau} \right\}, \end{aligned} \quad (17)$$



which holds for quadrupole molecules having the axial symmetry. Here,  $\Theta_{ij}$  is the angle between the axes of symmetry of the molecules of species  $i$  and  $j$ , respectively,  $g_{ij}(\tau)$  — the distribution function and  $\Omega^2 d\tau = d\mathbf{r}_{ij}^2 d\omega_i d\omega_j$ , where  $\Omega = \int d\omega_i$ . The quantities  $A_{\text{is}}^{(ij)}$  and  $A_{\text{anis}}^{(ij)}$  in the foregoing expressions account for the effect of the anisotropy of the molecular field on isotropic and anisotropic light scattering, respectively, and are given by

$$A_{\text{is}}^{(ij)} = \frac{1}{3} (\lambda_{\parallel}^{(i)} \psi_{\parallel}^{(i)} + 2\lambda_{\perp}^{(i)} \psi_{\perp}^{(i)}) + \frac{1}{3} (\lambda_{\parallel}^{(j)} \psi_{\parallel}^{(j)} + 2\lambda_{\perp}^{(j)} \psi_{\perp}^{(j)}) + \\ + \frac{1}{9} (\lambda_{\parallel}^{(i)} \psi_{\parallel}^{(i)} + 2\lambda_{\perp}^{(i)} \psi_{\perp}^{(i)}) (\lambda_{\parallel}^{(j)} \psi_{\parallel}^{(j)} + 2\lambda_{\perp}^{(j)} \psi_{\perp}^{(j)}), \quad (18)$$

$$A_{\text{anis}}^{(ij)} = \frac{\lambda_{\parallel}^{(i)} \psi_{\parallel}^{(i)} - \lambda_{\perp}^{(i)} \psi_{\perp}^{(i)}}{\lambda_{\parallel}^{(i)} - \lambda_{\perp}^{(i)}} + \frac{\lambda_{\parallel}^{(j)} \psi_{\parallel}^{(j)} - \lambda_{\perp}^{(j)} \psi_{\perp}^{(j)}}{\lambda_{\parallel}^{(j)} - \lambda_{\perp}^{(j)}} + \\ + \left( \frac{\lambda_{\parallel}^{(i)} \psi_{\parallel}^{(i)} - \lambda_{\perp}^{(i)} \psi_{\perp}^{(i)}}{\lambda_{\parallel}^{(i)} - \lambda_{\perp}^{(i)}} \right) \left( \frac{\lambda_{\parallel}^{(j)} \psi_{\parallel}^{(j)} - \lambda_{\perp}^{(j)} \psi_{\perp}^{(j)}}{\lambda_{\parallel}^{(j)} - \lambda_{\perp}^{(j)}} \right). \quad (19)$$

$H_{\text{is}}^{(ij)}$  and  $H_{\text{anis}}^{(ij)}$  account for the additional contribution to isotropic and anisotropic light scattering due to higher order effects such as hyperpolarizability of the molecules and polarizability of molecular quadrupoles. For these quantities we have:

$$H_{\text{is}}^{(ij)} = \frac{5}{2} \eta_{(i)} \kappa_{\text{is}}^{(i)} \frac{\gamma_{(i)} \Theta_{(i)}^2}{\alpha_{(i)}^{1/2}} + \frac{5}{2} \eta_{(j)} \kappa_{\text{is}}^{(j)} \frac{\gamma_{(j)} \Theta_{(j)}^2}{\alpha_{(j)}^{1/2}} + \dots, \quad (20)$$

$$H_{\text{anis}}^{(ij)} = \frac{7}{4} \eta_{(i)} \kappa_{\text{anis}}^{(i)} \frac{\gamma_{(i)} \delta_{\gamma(i)} \Theta_{(i)}^2}{\alpha_{(i)}^{1/2} \delta_{\alpha(i)}} + \frac{7}{4} \eta_{(j)} \kappa_{\text{anis}}^{(j)} \frac{\gamma_{(j)} \delta_{\gamma(j)} \Theta_{(j)}^2}{\alpha_{(j)}^{1/2} \delta_{\alpha(j)}} + \\ + \frac{1}{4} \xi_{(i)} \frac{B_{(i)} \Theta_{(i)}}{\alpha_{(i)}^{1/2} \delta_{\alpha(i)}} + \frac{1}{4} \xi_{(j)} \frac{B_{(j)} \Theta_{(j)}}{\alpha_{(j)}^{1/2} \delta_{\alpha(j)}} + \dots \quad (21)$$

Here

$$\delta_{\alpha(i)} = \frac{\alpha_{\parallel}^{(i)} - \alpha_{\perp}^{(i)}}{3\alpha_{(i)}} \quad \text{and} \quad \alpha_{(i)} = \frac{1}{3} (\alpha_{\parallel}^{(i)} + 2\alpha_{\perp}^{(i)}) \quad (22)$$

describe the anisotropy of polarizability of the isolated molecule of species “ $i$ ” and its mean polarizability, respectively, whereas

$$\delta_{\gamma(i)} = \frac{2(3\gamma_{\parallel}^{(i)} + 3\gamma_{\perp}^{(i)} - 4\gamma_{\perp}^{(i)})}{21\gamma_{(i)}}, \quad \gamma_{(i)} = \frac{1}{15} (3\gamma_{\parallel}^{(i)} + 12\gamma_{\perp}^{(i)} + 8\gamma_{\perp}^{(i)}) \quad (23)$$

are the anisotropy of hyperpolarizability of the molecule of species  $i$  and its mean hyperpolarizability.

The parameters  $\eta_{(i)}$ ,  $\xi_{(i)}$ ,  $\kappa_{\text{is}}^{(i)}$  and  $\kappa_{\text{anis}}^{(i)}$ , introduced in eqs. (20) and (21) are defined as follows

$$\eta_{(i)} = \frac{1}{10} \left( \frac{2\varepsilon + 1}{3\varepsilon + 2} \right)^2 \left( \frac{n_i^2 - 1}{n_i^2 + 2} \right)^{1/2} (\chi_{\perp}^{(i)^2} + 2\chi_{\parallel}^{(i)^2}), \quad (24)$$

$$\xi_{(i)} = \left( \frac{2\varepsilon + 1}{3\varepsilon + 2} \right) \left( \frac{n_i^2 - 1}{n_i^2 + 2} \right)^{2/3} (\chi_{\perp}^{(i)} + 2\chi_{\parallel}^{(i)}), \quad (25)$$

$$\kappa_{is}^{(i)} = \{15\gamma_{(i)} \overline{F_{i3}^2} - 2(3\gamma_{\parallel}^{(i)} + 4\gamma_{\perp}^{(i)}) (\overline{F_{i3}^2} - \overline{F_{i1}^2})\} \{5\gamma_{(i)} \overline{F_i^2}\}^{-1}, \quad (26)$$

$$\kappa_{anis}^{(i)} = \{21\gamma_{(i)} \delta_{\gamma(i)} \overline{F_{i3}^2} - 4(3\gamma_{\parallel}^{(i)} - 2\gamma_{\perp}^{(i)}) (\overline{F_{i3}^2} - \overline{F_{i1}^2})\} \{7\gamma_{(i)} \delta_{\gamma(i)} \overline{F_i^2}\}^{-1}, \quad (27)$$

wherein the mean square molecular fields  $\overline{F_{i1}^2}$ ,  $\overline{F_{i3}^2}$  and  $\overline{F_i^2}$  are given, for axially symmetric quadrupolar molecules, by:

$$\overline{F_{i1}^2} = \overline{F_{i2}^2} = \frac{9}{20} \left( \frac{2\varepsilon + 1}{3\varepsilon + 2} \right)^2 \left( \frac{n_i^2 - 1}{n_i^2 + 2} \right)^{2/3} \chi_{\perp}^{(i)} \frac{\Theta_{(i)}^2}{\alpha_{(i)}^{8/3}}, \quad (28)$$

$$\overline{F_{i3}^2} = \frac{9}{5} \left( \frac{2\varepsilon + 1}{3\varepsilon + 2} \right)^2 \left( \frac{n_i^2 - 1}{n_i^2 + 2} \right)^{2/3} \chi_{\parallel}^{(i)} \frac{\Theta_{(i)}^2}{\alpha_{(i)}^{8/3}}, \quad (29)$$

$$\overline{F_i^2} = 2\overline{F_{i1}^2} + \overline{F_{i3}^2} = 9\eta_{(i)} \frac{\Theta_{(i)}^2}{\alpha_{(i)}^{8/3}}. \quad (30)$$

In a former paper (Kielich 1960), when passing from the formulas (5.2) and (5.3) to eqs. (5.13) and (5.14), the simplifying assumption of  $\kappa_{is}^{(i)} = \kappa_{anis}^{(i)} = 1$  had been made. From the foregoing eqs. (26) and (27), this condition is seen to be satisfied strictly only if the molecular field possesses the spherical symmetry, i. e. if  $\overline{F_{i1}^2} = \overline{F_{i2}^2} = \overline{F_{i3}^2} = \frac{1}{3} \overline{F_i^2}$ . Assuming also  $\gamma_{\parallel}^{(i)} = \frac{1}{3} (\gamma_{\parallel}^{(i)} + \gamma_{\perp}^{(i)})$  (see, Buckingham and Stephen 1957), the quantities  $\delta_{\gamma(i)}$  and  $\gamma_{(i)}$  defined above by eqs. (23) reduce to

$$\delta_{\gamma(i)} = \frac{\gamma_{\parallel}^{(i)} - \gamma_{\perp}^{(i)}}{3\gamma_{(i)}}, \quad \gamma_{(i)} = \frac{1}{3} (\gamma_{\parallel}^{(i)} + 2\gamma_{\perp}^{(i)}) \quad (31)$$

which is identical with the expressions of (5.15) (Kielich, 1960).

Also, eq. (7.5) for the molecular refraction  $R_m$  was derived on the simplifying assumption of  $\kappa_{is}^{(i)} = 1$ . Without the latter, we have the general expression

$$R_m = \frac{4\pi}{3} N \sum_i x_i \alpha_{(i)} \left\{ 1 + \frac{1}{3} (\lambda_{\parallel}^{(i)} \psi_{\parallel}^{(i)} + 2\lambda_{\perp}^{(i)} \psi_{\perp}^{(i)}) + \frac{5}{2} \eta_{(i)} \kappa_{is}^{(i)} \frac{\gamma_{(i)} \Theta_{(i)}^2}{\alpha_{(i)}^{11/3}} \right\}, \quad (32)$$

which holds for axially symmetric quadrupolar molecules.

In the case of a one-component system, eqs. (16), (17) and (32) reduce to the form

$$F_{is} = 9\alpha^2 N \left\{ \left( 1 + \frac{\lambda_{\parallel} \psi_{\parallel} + 2\lambda_{\perp} \psi_{\perp}}{3} \right)^2 + 5\eta \kappa_{is} \frac{\gamma \Theta^2}{\alpha^{11/3}} \right\} \frac{RT\beta_T}{V}, \quad (33)$$

$$F_{anis} = 9\alpha^2 \delta_{\alpha}^2 N \left\{ \left( 1 + \frac{\lambda_{\parallel} \psi_{\parallel} - \lambda_{\perp} \psi_{\perp}}{\lambda_{\parallel} - \lambda_{\perp}} \right)^2 + \frac{7}{2} \eta \kappa_{anis} \frac{\gamma \delta_{\gamma} \Theta^2}{\alpha^{11/3} \delta_{\alpha}} + \frac{1}{2} \xi \frac{B\Theta}{\alpha^{8/3} \delta_{\alpha}} \right\} \left\{ 1 + \frac{1}{2} \int (3 \cos^2 \Theta - 1) \left[ g(\tau) - \frac{N}{V} \right] d\tau \right\}, \quad (34)$$

$$R_m = \frac{4\pi}{3} N\alpha \left\{ 1 + \frac{1}{3} (\lambda_{||} \psi_{||} + 2\lambda_{\perp} \psi_{\perp}) + \frac{5}{2} \eta_{is} \frac{\gamma \Theta^2}{\alpha^{11/3}} \right\}, \quad (35)$$

with  $R$  denoting the gas constant,  $T$ —the absolute temperature,  $\beta_T$ —the isothermal compressibility coefficient of the medium and  $V$ —its molar volume.

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## LETTERS TO THE EDITOR

## ON THE HIGH TEMPERATURE SUSCEPTIBILITY OF FERRIMAGNETICS AND ANTIFERRIMAGNETICS

BY BOGDAN FECHNER

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*(Received October 31, 1960)*

It is well known from statistical mechanics that the zero field susceptibility per atom is given by

$$\chi = \frac{kT}{N} \left( \frac{\partial^2 \log Z}{\partial H^2} \right)_{H=0}$$

Kramers has suggested an approximative method of evaluating the function  $\log Z$  by expanding it in ascending power series of the reciprocal temperature. The calculations were carried through for ferromagnetism and antiferromagnetism by Opęchowski (1937) and others, for spin  $1/2$  and by Van Vleck (1937), Brown and Luttinger (1955), Rushbrooke and Wood (1958) for arbitrary spin. It is natural to extend these calculations to the case of ferrimagnetism and antiferrimagnetism with arbitrary spin of magnetic atoms. In the present note we shortly report the results of these calculations.

We start with the Hamiltonian in the form

$$\mathcal{H} = -2 \sum_{\langle i,j \rangle} J_{ij} S_i S_j - g\beta H \sum_i S_i^z$$

which relates to an ordered crystal structure composed of two kinds of magnetic atoms.  $\langle i,j \rangle$  means that the summation is extended over all neighbouring lattice sites in which magnetic atoms are present. Using the procedure explained by Rushbrooke and Wood, we obtain the expansion in the form

$$\chi = \frac{g^2 \beta^2 \tilde{S}}{3kT} \sum_{n=0}^{\infty} \frac{a_n}{(kT)^n},$$

where  $\tilde{S} = n_A \bar{S}_A + n_B \bar{S}_B$ . The coefficients  $a_n$  are quantities requiring explicit calculations, the details of which will be published later. We give here only the general expressions for the  $a$  coefficients up to  $n = 3$  valid for any crystal structure composed of  $N_A = A$  and  $N_B = B$  atoms.  $N_A + N_B = N$  is the number of lattice sites occupied by magnetic atoms. Denoting the three kinds of exchange interactions by  $J_{AA}$ ,  $J_{BB}$  and  $J_{AB}$  we find

$$\begin{aligned} \chi_1 &= \frac{2}{3} \tilde{S}^{-1} \{n_A c_{AA} \bar{S}_A^2 J_{AA} + n_B c_{BB} \bar{S}_B^2 J_{BB} + 2n_A c_{AB} \bar{S}_A \bar{S}_B J_{AB}\}, \\ \chi_2 &= \frac{1}{9} \tilde{S}^{-1} \{n_A c_{AA} [4(c_{AA} - 1) \bar{S}_A - 3] \bar{S}_A^2 J_{AA}^2 + n_B c_{BB} [4(c_{BB} - 1) \bar{S}_B - 3] \bar{S}_B^2 J_{BB}^2 + \\ &\quad + 2n_A c_{AB} [2(c_{BA} - 1) \bar{S}_A + 2(c_{AB} - 1) \bar{S}_B - 3] \bar{S}_A \bar{S}_B J_{AB}^2 + \\ &\quad + 8n_A c_{AA} c_{AB} \bar{S}_A^2 \bar{S}_B J_{AA} J_{AB} + 8n_A c_{BB} c_{AB} \bar{S}_A \bar{S}_B^2 J_{BB} J_{AB}\}, \\ \chi_3 &= \frac{4}{135} \tilde{S}^{-1} \{n_A [2(5c_{AA}(c_{AA} - 1)^2 - 3c_{AA} - 30p_{3A}) \bar{S}_A^2 - 3(c_{AA}(5c_{AA} - 3) + 10p_{3A}) \bar{S}_A + \\ &\quad + 6c_{AA}] \bar{S}_A^2 J_{AA}^3 + n_B [2(5c_{BB}(c_{BB} - 1)^2 - 3c_{BB} - 30p_{3B}) \bar{S}_B^2 - 3(c_{BB}(5c_{BB} - 3) + \\ &\quad + 10p_{3B}) \bar{S}_B + 6c_{BB}] \bar{S}_B^2 J_{BB}^3 + n_A c_{AB} [4(5(c_{AB} - 1)(c_{BA} - 1) - 3) \bar{S}_A \bar{S}_B \\ &\quad - 3(5c_{BA} - 3) \bar{S}_A - 3(5c_{AB} - 3) \bar{S}_B + 12] \bar{S}_A \bar{S}_B J_{AB}^3 + \\ &\quad + 5n_A c_{AA} c_{AB} [4(c_{AA} - 1) \bar{S}_A - 3] \bar{S}_A^2 \bar{S}_B J_{AA}^2 J_{AB} + \\ &\quad + 5n_A c_{BB} c_{AB} [4(c_{BB} - 1) \bar{S}_B - 3] \bar{S}_A \bar{S}_B^2 J_{BB}^2 J_{AB} - 5n_A [(6p_{2A,B} + 3c_{AA} c_{AB}) + \\ &\quad + 4(2p_{2A,B} - c_{AA} c_{AB}(c_{BA} - 1)) \bar{S}_A] \bar{S}_A^2 \bar{S}_B J_{AA} J_{AB}^2 - \\ &\quad - 5n_B [(6p_{2B,A} + 3c_{BB} c_{BA}) + 4(2p_{2B,A} - c_{BB} c_{BA}(c_{AB} - 1)) \bar{S}_B] \bar{S}_A \bar{S}_B^2 J_{BB} J_{AB}^2 + \\ &\quad + 20n_A c_{AA} c_{BB} c_{AB} \bar{S}_A^2 \bar{S}_B^2 J_{AA} J_{BB} J_{AB}\}. \end{aligned}$$

Here  $\tilde{S}_i$  stands for  $S_i(S_i + 1)$  and  $n_A = N_A/N$ ,  $n_B = N_B/N$  are the concentrations of the two components. The  $p$ 's and  $c$ 's are structural parameters which have the following meanings:  $c_{AA}$  is the number of nearest  $A$  neighbours to an  $A$  atom,  $c_{AB}$  is the number of nearest  $B$  neighbours to an  $A$  atom etc.  $N_A p_{3A}$ ,  $N_A p_{2A,B}$ ,  $N_B p_{2B,A}$  and  $N_B p_{3B}$  are the numbers of triangles, the sides of which join neighbouring lattice sites occupied respectively by: three  $A$  atoms, two  $A$  and one  $B$  atoms, two  $B$  and one  $A$  atoms, three  $B$  atoms. The values of these parameters for a given structure can be obtained by direct counting on a model lattice. In the special case, when there is only one kind of atoms present ( $N_A = N$ ,  $N_B = 0$ ) our results reduce to those obtained by Brown and Luttinger (1955).

We have also obtained the series expansion of the inverse susceptibility

$$\chi^{-1} = \frac{3kT}{g^2 \beta^2 \tilde{S}} \sum_{n=0}^{\infty} \frac{b_n}{(kT)^n}$$



but the coefficients  $b_n$  will not be given here with respect to their complexity. They are connected with the  $a$  coefficients by the relations

$$b_0 = 1, \quad b_1 = -a_1, \quad b_2 = a_1^2 - a_2, \quad b_3 = 2a_1a_2 - a_1^3 - a_3.$$

The application of these results to ferrites and ferromagnetic alloys will be given in a subsequent paper.

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## ON A NEW TYPE OF CONDENSER FOR MEASURING THE DIELECTRIC PERMITTIVITY OF SOLIDS BY THE METHOD OF IMMERSION

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The "method of immersion" constitutes one of the most exact methods of measuring the dielectric permittivity of substances in the solid state. This method, first proposed by Starke (1897), is at present applied in all cases of a material accessible in the form of minute fragments only, such as powder or small fibres. It bases on the fact that the capacity of a condenser filled with liquid does not change if powder of the same dielectric permittivity is added to the liquid. Since it is practically impossible to chose the liquid so that it shall possess the same permittivity as the powder, the procedure in most cases is this: the condenser is filled in turn with liquids of different values of the permittivity and the powder investigated is added, after which the capacity of the system obtained is measured. The respective values will be greater or smaller than those for the condenser filled with pure liquids, according to whether the permittivity of the powder is greater or smaller than that of the liquid. By plotting the capacity values of the condenser with the pure liquids on the axis of abscissae, and their variations on addition of the powder on the axis of ordinates, a graph connecting the points is obtained that intersects the axis of abscissae at the point corresponding to the capacity of the condenser filled with a liquid of exactly the same permittivity as the powder. With a condenser previously calibrated, the permittivity of the powder investigated can be computed.

The new type of condenser built at this laboratory admits of the rapid and convenient determination of the capacity when filled with a pure liquid or with a mixture of liquid and powder. Essentially, it presents a system of two cylindrical condensers of approximately the same capacity, placed axially one on top of the other (Fig. 1). The metal plates ( $p$ ) are connected to the glass parts ( $g$ ) with "Araldit", a heat-tempered putty produced by "Ciba". The outer plates are earthed; the inner ones have special leads to the measuring device ( $i_I$  and  $i_{II}$ ). On removing the screw ( $s$ ), the powder is introduced and, subsequently, as much liquid as is needed for the mixture to fill condenser I and the pure liquid to fill condenser II is added. The capacity of condenser II with the pure liquid is now measured. The device is now reverted by  $180^\circ$  so that the powder is transferred from condenser I to II, and the

capacity of the latter filled with the mixture is measured. Adding a liquid of different permittivity to the condenser, we proceed similarly until the sign of the difference between the capacity of condenser II filled with the liquid and that of condenser I filled with the mixture changes. By the graphical method already described, the capacity is finally measured for a liquid possessing a permittivity value equal to that of the powder. Another procedure

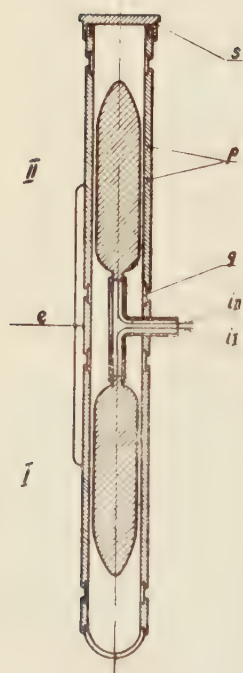


Fig. 1

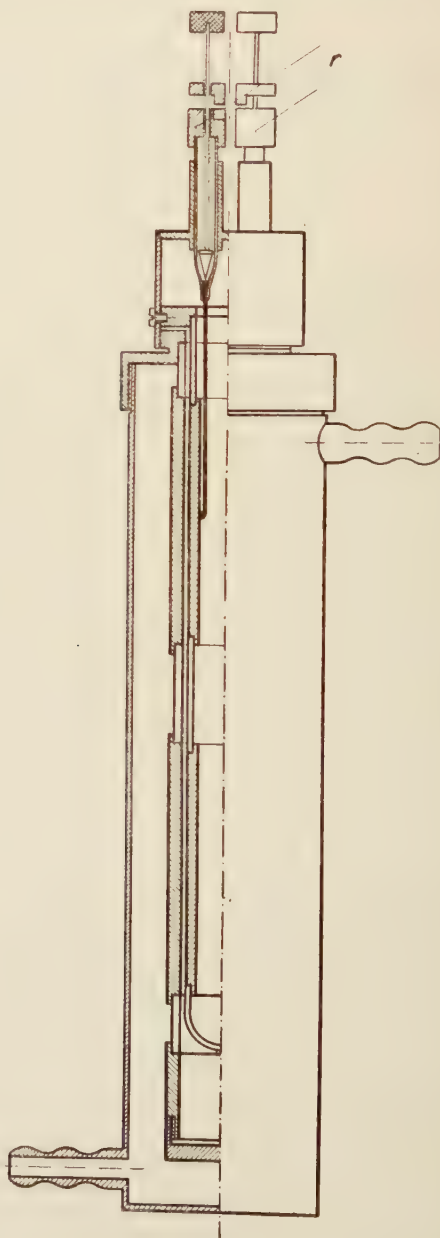


Fig. 2

is the following: if the capacities of the empty condensers I and II are known, these can be filled and the the permittivities of the liquids and of their mixtures with the powder computed. By plotting the permittivities of the liquids (abscissae) and the differences between the permittivities of the respective mixtures and those of the liquids (ordinates), a graph is obtained whence the permittivity of the powder is derived directly.

This type of condenser presents the additional advantage of eliminating error due to solubility of the powder in the liquid. Notwithstanding the fact that in such measurements liquids are used that do not dissolve the solid investigated noticeably, there is practically always some solubility, however small. Hence the use of a single condenser, whose capacity is measured once on filling it with the pure liquid and then on introducing the mixture, can give rise to error from the change in the dielectric properties of the liquid itself due to some amount of the powder in solution. In the present case, however, this can no longer occur, as the capacity is measured when the condenser is filled with a liquid that has already exerted whatever dissolving properties it possessed.

Moreover, a condenser was built for measurements of the the temperature dependence of the permittivity (Fig. 2). A system of two condensers remembling the one described is surrounded by a double-walled mantle circulating liquid of a temperature stabilized with a thermoregulator. Here, the condenser plates are provided by the walls of the hollow cylinders, through which leads pass from the internal plates. In order to avoid changes in the capacities of the leads, a system of fixed switches ( $r$ ) as described by Jeżewski (1955) is applied.

The foregoing types of condensers have been tested at this laboratory by Mr. Mieczysław Wierzbicki and Mrs. Teresa Morstin, who used solutions of nitrobenzene in benzene.

Starke, H., *Wied. Ann.*, **60**, 629 (1897); **60**, 804 (1897).

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## REVIEWS OF BOOKS

WILHELM H. WESTPHAL

*Physikalisches Praktikum*, Friedr. Vieweg & Sohn,  
Braunschweig 1959, 285 Seiten, Preis DM. 19,50.

*Physikalisches Praktikum* ist eine Sammlung von Beschreibungen praktischer Übungen aus dem Gebiete der Physik und ist als Hilfsmittel für die Studenten verschiedener Typen der Hochschulen vorgesehen.

Dieses Buch besteht aus zwei Hauptteilen. Im ersten kurzen Teil (25 Seiten) beschreibt der Verfasser die Grössen, die in den einzelnen Gebieten der Physik auftreten, die Methoden der Berechnung der Messungsergebnisse, gibt eine Reihe praktischer Hinweisungen und Regeln betreffs der Messungen. Auch die Fehlerrechnung ist kurz zusammengefasst. Die Aufgabe dieses Teiles des Buches ist die Studenten zur korrekten Ausführung und Deutung physikalischer Messungen vorzubereiten.

Zweiter Teil, beträchtlich länger (250 Seiten), enthält die eigentliche Beschreibung von 47 praktischer Übungen. Diese Übungen sind nach folgenden Gebieten der Physik eingeteilt: 1) Mechanik 2) Wärme, Gastheorie, Akustik 3) Optik 4) Elektrizität und Magnetismus. Am Ende des Buches sind Tabellen für manche physikalische Grössen in der Form der Diagramme angegeben.

Westphal's *Physikalisches Praktikum* hat sich besondere Stellung als Handbuch in der Praxis im physikalischen Laboratorium erworben. Es ist ein wichtiges Hilfsmittel besonders aus diesem Grunde, weil der Verfasser sich nicht nur zur Beschreibung der Praxis beschränkt, sondern auch die theoretische Einführung bei jeder Übung angibt. Es ist klar, dass die Theorie der Übungen nicht zu ausführlich sein kann, damit das Buch, welches den praktischen Charakter haben soll, nicht seine Klarheit verliere. Hier besteht aber eine gewisse Gefahr. Im allgemeinen muss die Theorie in einem praktischen Lehrbuch aus Notwendigkeit nur skizziert werden und für einen weniger orientierten Leser kann diese Tatsache den Eindruck einer allgemeinen Auffassung des Problems hervorrufen. Westphal's Buch hat eben diese Eigenschaft, dass es einen solchen Anschein nicht gibt, weil der Bereich des besprochenen Materials sich sehr eng mit dem Thema der Übung verbindet. Zugleich geht aber diese theoretische Einführung in die Einzelheiten des Problems ein und überschreitet oft das Niveau von meisten physikalischen Lehrbüchern für Hochschulen, so dass die Beschreibung des Problems nicht verengt wird. *Physikalisches Praktikum* hat noch einen Vorzug: nach der Besprechung jeder Übung folgt ein konkretes Zahlenbeispiel mit

den Diagrammen und der Diskussion der Fehler, was nicht nur zur besseren Verständigung des Themas beiträgt, sonder auch als Muster bei der Ausführung der Übungen dienen kann. Das hilft dem Studenten die fehlerfreie und systematische Arbeit im Laboratorium zu erlernen.

Das Buch hat aber auch einige Nachteile. Der Verfasser hat sich eng auf das Material der klassischen Physik beschränkt. Es handelt sich nicht natürlich um spezielle Übungen aus dem Gebiete der modernen Physik, z.B. aus der Kernphysik, aber um gewisse Gebiete, welche sich bestimmt in den Bereich der allgemeinen Physik einschliessen lassen. Es wurden hier z.B. das Photoeffekt, Optische- und Röntgenspektren und Vakuumtechnik in Betracht genommen. Andererseits sind im *Physikalischen Praktikum* Übungen besprochen, wie die Jolly-Waage, welche in der gegenwärtigen Praxis im Laboratorium keine Anwendungen finden und welche durch Übungen aus den oben erwähnten aktuellen Gebieten der Physik ersetzt werden können.

Obwohl der Bereich des Materials nicht ganz den modernen Bedürfnissen des Laboratoriums für Studenten entspricht, so gehört es doch zu den besten praktischen Lehrbüchern und deshalb darf dieses Buch in keinem Laboratorium für Studenten fehlen. Der beste Beweis der Vorzüge der guten Bearbeitung des Materials dieses Buches ist die Tatsache dass sie seit der Erscheinung (erste Ausgabe im Jahre 1937) schon neun Ausgaben hatte.

Man soll auch die besonders sorgfältige graphische Ausführung des Buches hervorzuheben.

Zofia Leś



## FRANK MATOSI

*Der Raman-Effekt*, Second revised edition. Friedr. Vieweg u. Sohn, Braunschweig 1959, 84 p., 24 figs., 9 tables.

Matossi's book was originally edited in the series „Verfahrens- und Messkunde der Naturwissenschaft“. Its primary aim was thus to present experimental and theoretical methods employed in Raman spectra investigations. Chapter 1 deals descriptively with the fundamentals of the effect, on the basis of the quantum model. In Chapter 2, the author considers in turn light sources, Raman spectrographs, methods of measuring the frequencies, intensities and degree of depolarisation of the lines, apparatus, and models yielding the oscillations of molecules. This last problem initiates Chapter 3 (applications); here, oscillation forms for molecules of various symmetry are derived theoretically, and the conclusions from Placzek's polarizability theory are discussed. The oscillations of organic molecules and of crystals are treated in some detail. Among the Tables, those of the oscillation types and oscillation type characters of molecules of various symmetry are noteworthy.

The second edition brings much new and valuable material not to be found in the first edition published 15 years ago. However, some of this fails to deal adequately with some of the most important contemporary problems in Raman techniques. In Chapter 1, a discussion of the resonance Raman effect has been added. Chapter 2, although now mentioning the Toronto type spiral lamp, is totally silent on other types of low-pressure lamps coming into use. Some mention is made of photomultiplier methods of spectrum recording; however, the author avoids dealing extensively with these growingly employed methods, and refers the reader to Brandmueller and Moser's article (*Z. angew. Physik*, **8**, 35, 142 (1956); **9**, 567 (1957)). A description of new types of Raman vessels is added (the multiple reflexion vessel, various micro-vessels) and the problem of measuring intensities given more place. However, only the difference between the maximum and integral intensity is mentioned, whereas no mention is made of the attempts at converting the experimental intensities into real intensities which are the basis for determining the symmetrical and anisotropic parts of the polarizability tensor. At the opening of Chapter 3, the second edition contains a discussion of the method of determining molecular oscillations by means of a system of oscillating electric circuits; but for this, Chapter 3 is almost unchanged.

With regard to the small volume, the problems are dealt with very concisely; the reader, however, will find 143 references to monographs, various collective publications, and to the more prominent original papers that appeared until the end of 1958. The style is uncomplicated, and is easily understood by the reader whose German is not high grade.

Matossi's book fails to give an account of the theoretical foundations of the Raman effect, whether classical or quantum. This is all the more to be regretted as the applications (Chapter 3) are of a predominantly theoretical character (the determination of oscillation forms) and are less preoccupied with direct chemical applications. There is not a single picture of a Raman spectrum to be found in the entire book. Besides, numerous papers by Soviet scientists, especially papers that have not been translated into the Western languages, are left unmentioned.

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